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Wastes from Manufacture of Dyes and Pigments: Volume 1. Azo Dyes and Pigments (Benzidine and Its Congeners Subsector)

SRI International, Menlo Park, CA

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WASTES FROM MANUFACTURE OF DYES AND PIGMENTS: VOLUME 1. AZO DYES AND PIGMENTS (Benzidine and Its Congeners Subsector)

By

D. C. Bomberger
R. L. Boughton

SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025

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Task 1

Project Officer
Mark J. Stutsman
Industrial Pollution Control Division
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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16. ABSTRACT

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The major components in the waste streams were identified, and the amounts produced were estimated. These estimates were made on an individual dye basis and summarized on an industry-wide basis. The major potential discharges of dye, unreacted intermediates, and reaction by-products are in the mother liquor after dye or pigment precipitation. Other major sources of solid residues included dye and pigments on baghouse fines and intermediates in discarded shipping containers.

Pigment manufacture represented the most important source of wastes because of its large volume relative to dyes. The emissions estimates showed 3,3'-dichlorobenzidine, o-dianisidine, and benzidine, were among the ten materials estimated to represent the major organic emissions from dye and pigment manufacture.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is one of a series of preliminary studies of segments of the dye and pigment manufacturing industry conducted for the Organic and Inorganic Chemicals and Products Branch of the Industrial Pollution Control Division. The objective of these studies was to determine if process waste streams might contain hazardous material and to recommend sites where a sampling program could be used to confirm the nature of any hazards that were identified.

David C. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

In a study of the manufacture of dyes and pigments based on benzidine and its congeners, several solid waste streams that could contain hazardous material were identified. The solid residues included filter cake from clarifying operations, intermediates on discarded shipping containers, and fines collected in bag houses used in grinding and drying operations. An aqueous waste stream containing process wastewater and mother liquor that could contain hazardous material was also identified.

The major components in the waste streams were identified, and the amounts produced were estimated. These estimates were made on an individual dye basis and summarized on an industry-wide basis. The major potential discharges of dye, unreacted intermediates, and reaction by-products are in the mother liquor after dye or pigment precipitation. These materials could remain an aqueous discharge or end up on waste water treatment solids. Other major sources of solid residues included dye and pigments on baghouse fines and intermediates in discarded shipping containers.

Pigment manufacture represented the most important source of wastes because of its large volume relative to dyes. The emissions estimates showed that three materials listed as being hazardous in the Resource Recovery and Conservation Act (RCRA) regulations (Federal Register, 1980), namely, 3,3'-dichlorobenzidine, o-dianisidine, and benzidine, were among the ten materials estimated to represent the major organic emissions from dye and pigment manufacture. 3,3'-Dichlorobenzidine is discharged from pigment manufacturing, whereas o-dianisidine and benzidine are discharged from dye manufacturing. Sampling at six representative manufacturers was recommended to determine actual waste composition and amount.

This report was submitted in fulfillment of Contract No. 68-03-2934 by SRI International under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period June 26, 1980, to September 21, 1981, and work was completed as of October 30, 1983.

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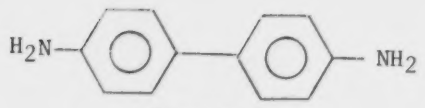
Section 1

INTRODUCTION

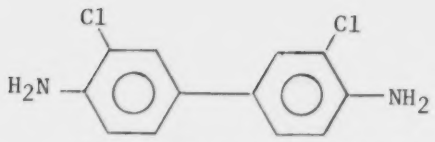
The Resource Conservation and Recovery Act (RCRA) requires that hazardous solid wastes produced by manufacturing operations be identified and disposed of in a manner that limits the release of hazardous materials to the environment. To date, a large number of specific waste streams from manufacturing processes have been listed in regulations as being hazardous because of their chemical composition. The objective of this preliminary study is to help determine if wastes produced by the manufacture of dyes and pigments in the United States require listing as hazardous materials. An analysis of both the chemistry and the physical processing involved in dye and pigment manufacturing will be used to identify all wastes that may contain significant chemical hazards. An analysis of the industry will be used to determine specific manufacturers where the candidate wastes are produced. This information will help the U.S. Environmental Protection Agency, Office of Solid Wastes, to design a sampling and analysis program to confirm or disprove the presence of hazardous materials in the candidate wastes and thereby develop a basis for listing dye and pigment manufacturing wastes under RCRA. This report deals with the wastes from the manufacture of azo dyes and pigments based on benzidine and its congeners.

Among the commonly recognized structural classes of dyes and pigments, the most important commercially in the United States are the azo dyes and pigments. The 1978 U.S. production of azo dyes and pigments was approximately 41,000 metric tons or about 35% of all U.S. dye and pigment production. These dyes and pigments are characterized by the presence of one or more azo groups (-N=N-) in the molecule. Consequently, the class can be divided into subclasses (monoazo, disazo, trisazo, tetrakisazo, and polyazo). A special subclass consists of azoic compounds; namely, azoic coupling components, azoic compositions, and azoic diazo components, that are reacted on the fiber to produce azo dyes. The azo dyes and pigments class can also be divided into groups of dyes and pigments produced from one common, structurally related group of starting materials. One such group of starting materials consists of those substituted biphenyls having amine groups in both para positions (i.e., benzidine and related compounds having additional substituents in the two rings). Theoretically, this group can include a very large number of compounds, but commercially significant dyes are produced from only a limited number of the compounds. The structures and common names of these compounds, henceforth called benzidine and its congeners, are presented on the next page.

The dyes and pigments produced in commercial quantities in the United States from these starting materials were selected as the subject of this initial study under this task of the contract because of the present concerns about their possible adverse effects on the environment and human health. The Colour Index numbers and names of these dyes and pigments (grouped according to dye type and the starting material used for their production) and the 1978 U.S. production levels reported in the Organic Dyes and Pigments Data Base prepared by SRI International (Swett et al., 1983) are shown in Table 1. For a



Benzidine



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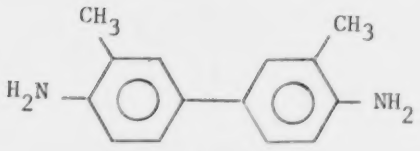
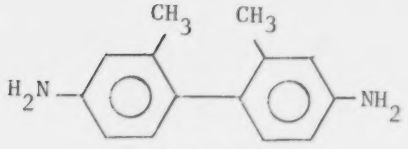
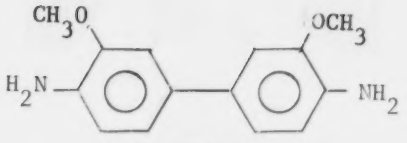


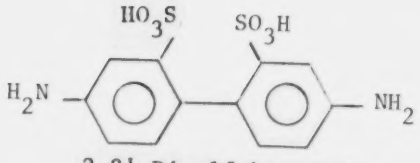
ortho-Tolidine



meta-Tolidine



ortho-Dianisidine



2,2'-Disulfobenzidine

number of dyes and pigments, production is shown only as greater than a minimum number. These are dyes and pigments produced by 3 or fewer manufacturers so that public sources do not list specific production amounts. The CICIS* data base lists production ranges for some of these dyes and pigments in its nonconfidential files. The production ranges cover an order of magnitude that does not always overlap the values shown in Table 1 which are derived from the U.S. International Trade Commission (1979). It seems reasonable to assume that, in general, however, production might be 10 times the value shown. The higher production values would not significantly change the ordering of the table.

In the following sections of this report the process chemistry of the azo dyes and pigments based on benzidine and its congeners and the sources of wastes during azo dye and pigment manufacture are discussed in detail. The final section gives the estimated amounts of solid residues and aqueous wastes produced during dye and pigment manufacture developed from the engineering analysis of Section 5.

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*Chemicals in Commerce Information System (CICIS) (Nonconfidential files of the TSCA Inventory). U.S. Environmental Protection Agency, Office of Pesticides and Toxic Substances, Washington, D.C.

Table 1

DYES AND PIGMENTS BASED ON BENZIDINE AND ITS CONGENERS INCLUDED IN THIS STUDY

	Colour Index No.	Color	1978 U.S. Production (metric tons/yr)
DIRECT DYES			
Benzidine-Based	30235	Black 38	373
	22590	Blue 2	99
	30295	Green 6	49
	--	Resin Flat Black WP	38
	30145	Brown 95	34
	30120	Brown 154	29
	22610	Blue 6	28
	35660	Brown 31	17
	22120	Red 28	17
	36300	Brown 74	15
	22311	Brown 2	13
	22130	Orange 8	12
	30245	Black 4	12
	22310	Red 1	12
	30280	Green 1	6
	30140	Brown 6	4
o-Dianisidine-Based	24401	Blue 218	445
	--	Blue 80	133
	23155	Blue 98	123
	24410	Blue 1	41
	24400	Blue 15	>10
	--	Blue 160	> 7.5
	24411	Blue 76	> 5
	--	Blue 100	> 5
	24140	Blue 8	> 2
	24175	Blue 151	> 2
o-Tolidine-Based	23500	Red 2	> 9
	23630	Red 39	> 7
	23797	Blue 25	> 5
	23850	Blue 14	> 2
	--	Brown 230	> 2
	23365	Orange 6	> 2

Table 1 (Continued)

	Colour Index No.	Color	1978 U.S. Production (metric tons/yr)
ACID DYES			
Benzidine-Based	22245	Red 85	18
Disulfobenzidine-Based	22890	Red 97	>5
	22910	Yellow 42	>2
m-Tolidine-Based	23266	Red 111	>2
o-Tolidine-Based	23635	Red 114	140
	--	Red 167	>5
PIGMENTS			
Dichlorobenzidine-Based	21090	Yellow 12	5,380
	21095	Yellow 14	1,420
	21105	Yellow 17	621
	21100	Yellow 13	232
	21110	Orange 13	108
	21115	Orange 34	38
	21120	Red 38	>7
	21096	Yellow 55	>1
o-Dianisidine-Based	21160	Orange 16	211
	21180	Blue 25	>5
	21200	Red 41	>1
AZOIC COUPLING COMPONENTS			
o-Dianisidine-Based	37575	3	>5
o-Tolidine-Based	37610	5	>2
AZOIC COMPOSITIONS			
	--	Blue 3	>10
	--	Black 4	>2
AZOIC DIAZO COMPONENT			
o-Dianisidine-Based	37235	48	>2

Section 2

SUMMARY AND CONCLUSIONS

In the preliminary study of dyes and pigments based on benzidine and its congeners, several residue streams were identified that might contain hazardous material. These included:

- Filter cake from clarifying operation after diatozation and coupling. The cake could contain unreacted intermediates, partially coupled dye molecules, N-nitrosamines, and chlorinated biphenyls. If the filter cake is treated with hypochlorite, as is the case at some plants, the total amount of organic material present may be reduced but additional chlorinated aromatics may be created. There was not enough information available to quantify this waste stream.
- Discarded shipping containers. These would be paper bags and fiber drums used to transport dye and pigment intermediates, and would contain a residual amount of intermediate when emptied.
- Wastewater treatment solids. The evidence suggests that the solids will be contaminated with low levels of all of the dye and pigment intermediates as well as the dyes and pigments themselves and some reaction by-products. If these solids are land-filled, benzidine and its congeners and other intermediates may be released due to reduction of the azo linkages under the anaerobic conditions prevailing in the landfill.
- Baghouse fines. The fines are generated during the drying, sizing, standardizing, and packaging of the dyes and pigments. The fines will be principally the dyes and pigments and inert salts. Anaerobic conditions in a disposal site could cause benzidine and its congeners as well as other intermediates to be released from these fines.

On an industry-wide basis, the major sources of waste emissions are associated with pigment manufacture rather than dye manufacture simply because pigments are the major products produced from benzidine and its congeners. At any given plant, the major source of discharges of organic chemicals is probably the process wastewater rather than the solid residue stream, since, at many locations, the process wastewater includes the mother liquor that contains unreacted intermediates and by-products in potentially high concentrations. Actual emissions will,

however, be quite site-specific, since emissions will be affected by the disposition of the mother liquor, specific treatment of individual process step wastewaters, the overall wastewater treatment system, and the treatment of the filter cakes. The intermediate and by-product emissions that are summarized in Section 6 (Tables 7 and 10) ignored these site specific factors.

The information on the production patterns for dyes and pigments contained in Section 6 (Tables 7 and 9) was analysed to choose a few representative manufacturers where a sampling program might be conducted to confirm the composition and the magnitude of the estimated waste emissions. Companies were chosen where the major volume dyes and pigments based on benzidine, 3,3'-dichlorobenzidine, o-tolidine, and o-dianisidine were manufactured. There was no way to determine exactly how much of each dye or pigment was made at each manufacturing site, so it was assumed that each site producing a major dye or pigment produced a signficant fraction of the total amount produced.

For determining benzidine waste emissions, there is only one company: Fabricolor Incorporated. Both Sterling Drug Inc. (Hilton-Davis Chemical Co.) and Sun Chemical Corporation (Pigments Division) manufacture the major pigments based on 3,3'-dichlorobenzidine and are, therefore, logical candidates for a sampling program. Atlantic Chemical Corporation, Crompton & Knowles Corporation (Dyes and Chemical Division), and Toms River Chemical Corporation are all producers of the major dyes based on o-tolidine and o-dianisidine and appear to be logical candidates for a sampling program.

The six companies that are recommended for a sampling program should yield samples from facilities using different manufacturing and waste treatment practices. Since there is considerable overlap in the actual dyes or pigments that they make, the six company sampling program increases the chances of identifying material in the waste streams that may be sensitive to plant practices.

Section 3

PROCESS CHEMISTRY

INTRODUCTION

A discussion of the process steps required to synthesize the azo dyes and pigments, based on benzidine and its congeners, will aid in formulating the emission estimates developed in Section 5. The first part of this section describes the azo dyes and pigments use classes as background. The remainder of the section is devoted largely to a discussion of the process chemistry of the two key steps required to synthesize these dyes and pigments, diazotization and coupling, with special attention given to the starting materials, intermediates, reaction conditions, and potential by-products. The recipe for an azo dye is shown in detail in Appendix A. Some azo dyes and pigments are produced by reactions other than diazotization and coupling and these reactions are briefly discussed.

The dyes and pigments produced commercially from benzidine and its congeners fall into the following three major classes:

- Direct dyes
- Acid dyes
- Pigments.

In addition, small amounts of azoic compounds (azoic coupling compounds, azoic diazo components, and azoic compositions) are produced.

The class of direct dyes consists of anionic dyes substantive to cellulose when applied from an aqueous bath containing an electrolyte. Chemically, these dyes are mostly di-, tri-, and polyazo compounds (such as the dyes based on benzidine and its congeners), but monoazo, stilbene, oxazine, thiazole, and phthalocyanine compounds are also included.

Acid dyes are water-soluble anionic dyes applied to nitrogeneous fibers (e.g., wool, silk, nylon, and modified acrylics) that function by virtue of the presence of one or more sulfonic acid or other acidic

groups in the molecule. Chemically, these dyes consist of azine, azo (such as those based on benzidine and its congeners), anthraquinone, ketonimine, nitro and nitroso, triphenylmethane, and xanthene dyes.

Included in organic pigments are substances (usually insoluble in organic solvents) that impart a positive color to another substance (as opposed to whiting agents, extenders, and fillers). The principal chemical classes represented are azo compounds (including those based on benzidine and its congeners), polycyclic compounds, phthalocyanines, dioxazines, and triarylmethanes.

The class of azoic compounds includes those materials used to produce insoluble azo dyes in situ, usually on a textile substrate. The three subclasses consist of the azoic diazo components, azoic coupling components, and azoic compositions, which are mechanical mixtures of the first two in which the azoic diazo component has been stabilized to prevent coupling before application. The azoic diazo components consist of diazonium salts (or their parent amines when the dyer carries out the diazotization) based on aromatic amines (such as benzidine and its congeners). The azoic coupling components are principally beta-naphthol derivatives, but also include arylamides such as those made from benzidine and its congeners.

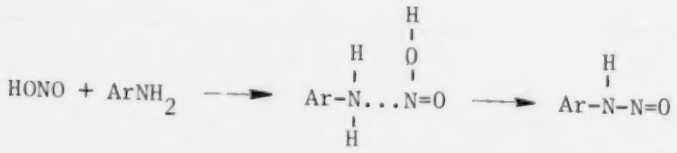
Certain structural features are required in the molecule for satisfactory performance in these use areas so the process chemistry differs somewhat for these classes. However, most of the synthesis routes include two key steps, diazotization and coupling. This section is devoted largely to a discussion of the process chemistry of these two steps, with special attention given to the starting materials, intermediates, reaction conditions, and potential by-products. The chemistry of azoic compounds is also discussed. A few acid dyes require esterification reactions that are discussed briefly.

Diazotization

As applied in dye chemistry, diazotization is the conversion of an aromatic amine to the corresponding diazonium chloride using nitrous acid (since nitrous acid is unstable, it is produced as needed from the reaction of aqueous solutions of sodium nitrite and hydrochloric acid at 0°C):

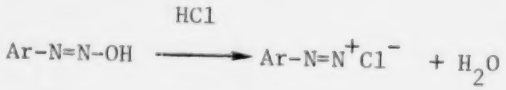
$$\underset{\text{Aromatic Amine}}{ArNH_2} + NaNO_2 + 2HCl \rightarrow \underset{\text{Diazonium Chloride}}{ArN{=}N^{+}Cl^{-}} + NaCl + 2H_2O$$

The mechanism of the diazotization reaction was elucidated by Hughes (1958). Nitrous acid reacts with the primary amine by attachment of the nitroso group to the nitrogen:

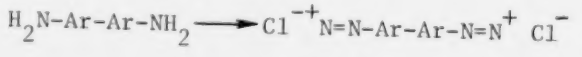


The product is unstable and isomerizes to a diazotic acid:

The diazotic acid is unstable in neutral or acid solution and usually decomposes rapidly to a diazonium salt:



When diazotization is applied to diamines such as benzidine and its congeners, both amino-groups are diazotizated so the process, termed tetrazotization, produces a tetrazonium chloride:



The tetrazotization is generally carried out at 0°-5°C for one to three hours using a molar ratio of diamine:sodium nitrite:hydrochloric acid of 1:2:3. The reaction product is an aqueous solution containing approximately 15% of the diazonium chloride and 7% sodium chloride.

The tetrazotization reportedly gives high yields (Abrahart, 1968; Lubs, 1955), so very little of the starting diamine is believed to be left in the reaction product. Some undecomposed diazotic acid (Ar-N=N-OH) may also be present. One source (Roberts, 1964) has indicated that the use of hydrochloric acid may result in the formation

of aryl chlorides as a result of the decomposition of the diazonium salt to nitrogen gas and a carbonium ion and reaction of the latter with chloride ion:

$$ArN{=}N^{+}Cl^{-} \longrightarrow N_2 + \left[Ar^{+} + Cl^{-}\right] \longrightarrow ArCl$$

If the tetrazonium salt of benzidine or its congeners underwent this decomposition, the aryl chloride would be a polychlorinated biphenyl.

The aryl chlorides are considered "terminated" by-products because they cannot be converted to the desired azo compounds in subsequent coupling steps and may occur during any step of the dye synthesis. They are not completely inert, however, and may react with the original primary amine starting material to form secondary amines, which in turn, may be converted by nitrous acid to their N-nitroso derivatives:

$$ArCl + ArNH_2 \longrightarrow HCl + ArNHAr \xrightarrow{HNO_2} Ar_2N{-}N{=}O$$

N-nitrosamines are very weak bases and are characteristically yellow or orange-yellow. An insoluble yellow liquid or solid N-nitroso compound separates from solution and, if formed during a diazotization reaction, the liquor may require clarification by filtration before transfer to the coupling reactor. This operation may be done only as required, although clarification is specifically called for in some dye recipes (BIOS, 1945). It is noteworthy that clarification was called for in every tetrazotization reaction mixture of Allied Chemical Co., which previously was a major manufacture of benzidine-based dyes (Keinath, 1976).

Since aromatic diamines such as benzidine and its congeners can undergo the above-described side reactions at one or both amino-groups, possibilities exist for the formation of a wide variety of by-products.

Because of the instability of the diazonium salts, the time that they exist in solution before coupling is held to a minimum. Many of the salts are explosive in the dry state; however, the various process steps are done in solution, and only traces of diazonium salts are present in the dye or the supernatant liquid at the end of the processing.

Coupling

As applied in azo dye manufacture, coupling is the conversion of a diazonium salt (the diazo component) to an azo compound by reaction with a aromatic compound (the coupling component), which generally has a strong electron-donating substituent on the aromatic ring (e.g., a phenolic, amino, or substituted amino group):

$$\underset{\text{Diazo Component}}{Ar\text{-}N{=}N^{+}Cl^{-}} + \underset{\text{Coupling Component}}{Ar'\text{-}H} \longrightarrow \underset{\text{Azo Compound}}{Ar\text{-}N{=}N\text{-}Ar'} + HCl$$

For the tetrazonium chlorides made from diamines such as benzidine and its congeners, the initial desired reaction may be either coupling of both diazonium chlorides or coupling of only one. In the latter case, the resultant product may be coupled again with a different coupling component. (An example of this latter procedure is discussed in Appendix A.) The final products from the two different procedures are the symmetrical and unsymmetrical azo compounds

$$Ar'\text{-}N{=}N\text{-}Ar\text{-}Ar\text{-}N{=}N\text{-}Ar' \qquad Ar'\text{-}N{=}N\text{-}Ar\text{-}Ar\text{-}N{=}N\text{-}Ar''$$

A variety of coupling components are used to produce the commercially significant dyes and pigments based on benzidine and its congeners (see Table 2 for a few examples). The specific chemicals used for each of the dyes and pigments are given in Section 6. The structures of these coupling components depend on the color desired and whether the material is going to be a direct or acid dye or a pigment. For direct and acid dyes, the molecules contain solubilizing groups such as hydroxyl, sulfonic acid, or carboxylic acid groups, whereas for pigments these groups mainly are absent. The direct dye molecule is designed to be long and have aromatic components that are coplanar, whereas the acid dye molecule is more compact.

Coupling is generally conducted under mildly alkaline conditions at 0-5°C for 4 to 24 hours, using an almost 1:2 molar ratio of

Table 2

EXAMPLES OF COUPLINGS USED FOR DYES AND PIGMENTS

Tetrazonium Chloride From:	Coupling Components		Dye or Pigment
	First Coupling	Second Coupling	
Benzidine	Naphthionic acid		Direct Red 28
Benzidine	Salicylic acid	Naphthionic acid	Direct Orange 8
o-Tolidine	Naphthionic acid		Direct Red 2
o-Dianisidine	N-Phenyl-7-amino-4-hydroxy-2-naphthalene sulfonic acid	1-Hydroxy-3,8-naphthalene disulfonic acid	Direct Blue 98
2,2'-Disulfobenzidine	2-Naphthol		Acid Red 97
3,3'-Dichlorobenzidine	Acetoacetanilide		Pigment Yellow 12

tetrazonium salt to coupling component when both diazonium salts are to be coupled and an almost 1:1 ratio when only one is to be coupled. Coupling reactions are carried out in a medium in which the equilibria of the diazo and the coupling components lie as far as possible toward the coupled product. For all coupling reactions, however, high pH is avoided to minimize noncoupling reactions. There is an optimum pH region for coupling reactions for each combination of diazo and coupling components. This region is about pH 4 to 9 for aromatic amines, 7 to 9 for enols and 8.5-9.5 for phenols. The rate of the coupling reaction for amines increases with increasing pH. However, lower pHs are used to suppress the formation of triazene compounds.

$$ArN_2^+Cl^- + Ar'NH_2 \underset{HCl}{\overset{NaOH}{\rightleftharpoons}} Ar\text{-}N{=}N\text{-}\overset{H}{\underset{|}{N}}\text{-}Ar' + H_2O + NaCl$$

The pH is adjusted using soda ash so that the hydrochloric acid by-product from the coupling is converted to sodium chloride.

A review of dye recipes given in the BIOS reports (1945) shows that in many cases excess ingredients are called for. Following the BIOS receipes will lead to an excess use of intermediates of up to 10% of the stoichiometric requirement for the o-tolidine and o-dianisidine dyes and the dichlorobenzidine pigments. The benzidine-based dye recipes called for 3-8% excess benzidine for some couplings and 7-15% excess coupling agent for others. It has been assumed for this assessment that 5% excess of each coupling agent, with respect to benzidine (or its congeners), is used during dye or pigment manufacturing. This excess should result in very little unreacted benzidine or its congeners at the end of the production sequence.

At the temperatures used for coupling, the reaction is reported to give almost quantitative conversion (90%-99%) to the desired azo compound (Rys and Zollinger, 1972; Lubs, 1955). However, impurities already present in the tetrazonium chloride can form side products, and the tetrazonium chloride can decompose (to form additional impurities) before coupling is completed. For example, (1) the salt

from ortho-tolidine is reported to couple slower than salts from benzidine or ortho-dianisidine and (2) phenol and G Acid (2-hydroxy-6,8-naphthalene disulfonic acid) are relatively slow couplers (Lapp et al., 1979). Manufacturing dyes and pigments based on these materials will yield more by-products than some other dyes. Venkataraman (1952) reports that the coupling reaction with one diazonium group on benzidine tetrazonium chloride deactivates the remaining diazonium group so that the second coupling reaction takes place more slowly than the first. It is assumed that the same is true for the benzidine congeners. This means that by-product-forming reactions are more likely in the latter stages of a dye or pigment synthesis than in the early stages.

If the diazonium chloride decomposes to nitrogen gas and a carbonium ion in a basic medium, the carbonium ion may react with hydroxyl ion to form phenols:

$$ArN{=}N^{+}Cl^{-} \longrightarrow N_2 + \left[Ar^{+} + Cl^{-}\right] \xrightarrow{NaOH} ArOH + NaCl$$

These phenols are considered "terminated" by-products because they cannot be converted to the desired azo compounds and may occur during any step of the dye synthesis.

In summary, coupling reactions are a competition between coupling and decomposition of the diazonium salts to form terminated by-products. In addition, partially coupled tetrazonium salts may remain. Because the diazonium chloride is not stable, only the terminated compounds would be expected to exist after a period of time.

Any diazotic acid formed in the diazotization step that does not decompose to the desired diazonium chloride may react in the basic solution used for most coupling reactions to form stable diazotate salts:

$$Ar{-}N{=}N{-}OH + NaOH \longrightarrow Ar{-}\underset{\displaystyle Na}{\underset{|}{N}}{-}N{=}O + H_2O$$

These salts are insoluble in water and may require that the coupling reaction liquor be clarified by filtration before proceeding to the next processes.

Other By-Products

Most of the potential by-products of the dye chemistry identified in the previous discussion have not been positively identified. Compounds that have been identified include 4-aminobiphenyl and 2,4-diaminoazobenzene, which were identified as contaminants in Direct Black 38, the major direct dye produced from benzidine (Nony, 1979). Diphenyline and semidine are known impurities of benzidine (Kirk-Othmer, 1978), and quinone and hydroquinone are known oxidation products of benzidine (Kirk-Othmer, 1978) that may be present in benzidine or dye and pigment manufacturing wastes that have been exposed to oxidative conditions.

Chemistry of Azoic Compounds

The azoic compounds, which include azoic diazo components, azoic coupling components, and azoic compositions, are dye intermediates that are used to produce colors directly on fibers. Azoic diazo components are either diazonium salts or aromatic amines that can be converted to diazonium salts in the dye bath and coupled to other aromatic molecules to produce a dye. The only currently produced azoic diazo component related to benzidine and its congeners is o-dianisidine.

Azoic coupling components react with diazonium salts in the dye bath or on the fibers to form dyes. The azoic coupling components related to benzidine and its congeners are complex organic molecules made by reacting the amino group in ortho-dianisidine or ortho-tolidine with organic acids or other acylating agents. Thus Azoic Coupling Component 3 is formed by reacting both amino groups in ortho-dianisidine with 3-hydroxy-2-naphthoic acid. Azoic Coupling Component 5 is formed by reacting one amino group of ortho-tolidine with ethyl acetoacetate and the other with ketene dimer.

The azoic compositions are mixtures of diazonium salts and azoic coupling components. The mixture itself is placed in the dye bath, where the coupling reactions to produce a dye occur. The components of the two azoic compositions related to benzidine and its congeners are not reported in public sources.

Esterification Reactions

Three acid dyes based on benzidine and its congeners acquire a final aromatic ring through an esterification reaction instead of a coupling via an azo group. They are: Acid Red 85, Acid Red 111, and Acid Red 114. p-Toluene sulfonyl chloride reacts with the hydroxyl group on a phenol molecule previously coupled to the dye molecule. Hydrogen chloride is a by-product of the reaction:

$$\underset{}{Ar\text{-}SO_2Cl} + \underset{\text{Partial dye molecule}}{HO\text{-}Ar'} \longrightarrow ArSO_2\text{-}OAr' + HCl$$

This reaction was not studied in detail because the dyes involved are relatively minor and not likely to produce significant amounts of hazardous wastes. It was assumed that excess p-toluene sulfonyl chloride was required and that the major reaction by-product was the ester of p-toluenesulfonyl chloride with excess phenol from the previous coupling step.

Section 4

DYE INTERMEDIATES

A list of the intermediates used in manufacturing dyes and pigments based on benzidine and its congeners in the United States was compiled from information in the Colour Index. Intermediates used to manufacture dyes and pigments whose ingredients were not published in the Colour Index could not be included in the list. Table 3 lists the organic intermediates for which some physical property data was found in computerized data bases such as OHMTADS* and published sources. (These physical properties are listed because they are used later in this report to discuss the emissions of intermediates during the dye manufacturing process.)

All the intermediates listed in Table 3 except the liquids, aniline and ethyl chloride, have melting points above ambient temperature, which means that they will be solids when received at the dye manufacturing site. All the compounds except ethyl chloride are estimated to have low vapor pressures (assumed to mean < 1 mm Hg at low temperatures). Some are reported to have substantial vapor pressures at high temperatures, but when the vapor pressure versus temperature data are extrapolated to ambient temperatures, the result is an insignificant vapor pressure. Thus, even though 2-naphthol has a vapor pressure of 100 mm Hg at 206°C, its vapor pressure will be far less than 1 mm Hg at 20°C. The low vapor pressures are mirrored in the high boiling points for all the compounds.

The low vapor pressures mean that vapor losses from manufacturing steps at ambient temperature will be minor. Even at 100°C, most of the

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*OHMTADS is an online data system that is a component of the Chemical Information System (CIS) operated by the National Institute of Health and the U.S. Environmental Protection Agency.

Table 3

PHYSICAL PROPERTIES OF INTERMEDIATES USED IN DYES AND PIGMENTS BASED ON BENZIDINE AND ITS CONGENERS

	Vapor Pressure (mmHg, °C)		Solubility in Water (ppm at 25°C)	Octanol-Water Partition Coefficient[a]	K_{oc}[b] 25°C	MP (°C)	BP (°C)
Benzidine and its Congeners							
Benzidine	Low	20	400[d]	1.34	<10	128	400
o-Tolidine	Low	20	Slightly[d]	--	<10	131	DEC[c]
o-Dianisidine	Low	20	Slightly[d]	--	<10	137	DEC
3,3'-Dichlorobenzidine	Low	20	Insoluble[d]	--	<100	132	DEC
m-Tolidine	Low	20	Insoluble[d]	--	<10	108	DEC
2,2'-Disulfobenzidine	Low	20	Slightly[d]	--	<10	175	DEC
Other Intermediates							
Salicylic acid	1	114	2000	2.23	3.0	158	DEC
Resorcinol	20	168	10^5	.78	0.02	111	281
2-Naphthol	100	206	1000	2.80	5.1	123	291
Aniline	<1	25	35,000	.92	0.32	-6	184
Phenol	80	86	6700	1.50	1.2	43	182
Ethyl chloride	1520	33	4500	1.43	1.6	-138	12
p-Nitroaniline	0.01	106	800	1.39	6.1	148	322
2,4-Diaminotoluene	1	100	Very high	--	<0.01	99	292
m-Phenylenediamine	1	100	3×10^5	--	--	63	287
Acetoacetanilide	0.01	20	Slightly	--	--	86	DEC

SOURCE: OHMTADS, unless otherwise noted.

[a] Hansch, 1978.

[b] K_{oc} indicates the tendency of organic chemicals to adsorb to the organic material in soils and sediments.

[c] DEC = decomposes.

[d] Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., Vol. 3. John Wiley and Sons, New York, 1978).

compounds have vapor pressures far less than water. Any of these low vapor pressure unreacted intermediates that accompany precipitated and filtered dye or pigment will volatilize much more slowly than water during the final product drying step. They will therefore remain on the dye or pigment after all of the water has evaporated.

Table 3 also gives octanol-water partition coefficients and K_{oc} values for some of the compounds. The octanol-water partition coefficients are low, indicating that the compounds are not likely to concentrate in lipid materials. K_{oc}, which indicates the tendency of organic chemicals to adsorb to the organic material in soils and sediments, is an important parameter for assessing the behavior of materials in the environment (Smith et al., 1977, 1978). It has been shown that for organic chemicals the overall potential for adsorption to soil and sediment is the product of K_{oc} and the fraction of the soil or sediment that is organic (Kenaga and Goring, 1978). All the compounds with known K_{oc} values listed in Table 3 have K_{oc} values less than 100, which in our experience (Smith et al, 1977, 1978) indicates that sorption to the organic material in soils and sediments will probably be very weak.

The solubility data in Table 3 are hard to interpret because it was not possible, given the scope of this study, to go back to the individual data sources. It is assumed, however, that "slightly" indicates solubilities in the range of 100 ppm and that "moderate" indicates solubilities in the range of 1000 ppm. Of the compounds listed, only aniline, resorcinol, 2,4-diaminotoluene, and m-phenylenediamine have substantial solubilities. This probably means that, during the final steps of the dye manufacturing process when the dye is salted out of solution, some unreacted intermediates could also salt out and remain with the product dye.

Table 4 lists the more highly substituted organic intermediates used in the United States to manufacture dyes and pigments based on benzidine and its congeners. No physical property data were found for these compounds in the sources searched. They are assumed to have properties similar to those in Table 3, that is, low vapor pressure, solid at ambient temperature, and not strongly adsorbed to organic material or

Table 4

OTHER INTERMEDIATES USED IN DYE AND PIGMENT MANUFACTURE
BASED ON BENZIDINE AND ITS CONGENERS

1-amino-8-hydroxy-3,6-naphthalene disulfonic acid (H acid)

1,8-dihydroxy-3,6-naphthalene disulfonic acid (Chromotropic acid)

4-amino-5-hydroxy-1,3-naphthalene disulfonic acid (Chicago acid)

1-hydroxy-3,6-naphthalene disulfonic acid

1-hydroxy-3,8-naphthalene disulfonic acid

4,8-diamino-2,6-naphthalene disulfonic acid

2-hydroxy-6,8-naphthalene disulfonic acid (G acid)

6-amino-4-hydroxy-2-naphthalene sulfonic acid (gamma acid)

1-amino-4-naphthalene sulfonic acid (Naphthionic acid)

1-amino-6-naphthalene sulfonic acid (1,6 Cleve's acid)

1-amino-7-naphthalene sulfonic acid (1,7 Cleve's acid)

7-amino-4-hydroxy-2-naphthalene sulfonic acid (J acid)

N-phenyl-7-amino-4-hydroxy-2-naphthlene sulfonic acid (N-phenyl-J-acid)

3-hydroxy-2-naphthalene carboxylic acid

3-hydroxy-2-naphthanilide

1-hydroxy-4-naphthalene sulfonic acid

o-acetoacetanisidide

o-acetoacetotoluidide

p-acetoacetotoluidide

2,4-acetoacetoxylidide

4-aminobenzene sulfonic acid (sulfanilic acid)

2-amino-1-phenol-4-sulfonic acid

2,4-diaminobenzene sulfonic acid

4,6-diamino-m-toluene sulfonic acid

ethyl acetoacetate

3-methyl-2-hydroxy-benzoic acid (2,3-cresotic acid)

3-methyl-1-phenyl-5-pyrazolone

3-methyl-1-p-tolyl-5-pyrazolone

o-phenylsulfonyl-2R acid

3-carbethoxy-1-phenyl-5-pyrazolone

soils and sediments. Because many of these compounds have multiple sulfonic acid and/or hydroxyl functional groups, they may be more soluble than the intermediates listed in Table 3.

SECTION 5

SOURCES OF WASTE DISCHARGES DURING DYE AND PIGMENT MANUFACTURE

The wide range of dye and pigment production processes and the specific plant characteristics and process control capabilities make estimation of material losses during dye manufacture a difficult task. In general, though, the most significant material losses will be intermediates that do not react and by-products such as incomplete dye or pigment molecules. These chemicals will be present either in the product or in the plant wastewater. The material in the wastewater may be discharged in the plant effluent (although some will be destroyed by treatment as described below), and some will be discharged on wastewater treatment solids.

Keinath (1976) has presented useful information concerning the presence of benzidine in the wastewaters of several unit operations of dye production. This information along with other published information (e.g., Steadman, 1977; Lapp, et al., 1976; Abrahart, 1968; Boeniger, 1980: NIOSH, 1980) and industry contacts has been used to develop materials release estimates for benzidine and its congeners, other intermediates, by-products, and dyes and pigments in the dye and pigment manufacturing processes.

This section first gives a general overview of dye and pigment production processes and then describes the bases used for developing estimates of the amounts of material lost (expressed as a percentage of the finished and standardized dye or pigment). The losses from both dye and pigment manufacture are discussed below according to the stages of production in which they would occur, (i.e., raw material receiving or product finishing, drying, grinding, standardization, blending, and packaging).

The solid residues are assumed to be placed in a landfill, either on the manufacturing property or at a commercial facility. The aqueous wastes are processed through a wastewater treatment system which may include physical, chemical and/or biological treatment of all or just some of the wastes. In some cases, the wastewater treatment system may discharge partially treated wastewater to municipal treatment systems. Concentrated waste streams may also be concentrated further and landfilled. The actual environmental releases that occur after wastewater treatment are discussed at the end of the section.

OVERVIEW OF DYE AND PIGMENT PRODUCTION PROCESSES

Figure 1 illustrates the dye and pigment manufacturing process and shows where the losses of all materials occur. The dye manufacturing equipment required to produce azo dyes and pigments consists of well stirred tanks, plate and frame filter presses, tunnel dryers or vacuum tray dryers, grinders, and blenders.

A dye or pigment plant is operated batchwise and typically contains several reactor trains. Each train includes at least one diazotization reactor, one coupling reactor, and one filter press. Complex dyes and pigments may require use of several reactor trains. Production of colors is usually rotated by set schedules from light to dark colored dyes.

After diazotization and coupling are completed, as described in Section 3, the dye materials are precipitated (salted out) by the addition of salt to give a final brine concentration of up to 20% weight by volume (BIOS, 1945, Abrahart, 1968). Pigments are insoluble and do not require salting out. The resulting slurry is filtered using a filter press, and air is blown through the press cake to remove as much mother liquor as possible (Kent, 1974). The cake is removed from the press and dried in an atmospheric tunnel dryer or a vacuum tray dryer. The dye is then ground in a swing hammer mill and thoroughly mixed in a blender.

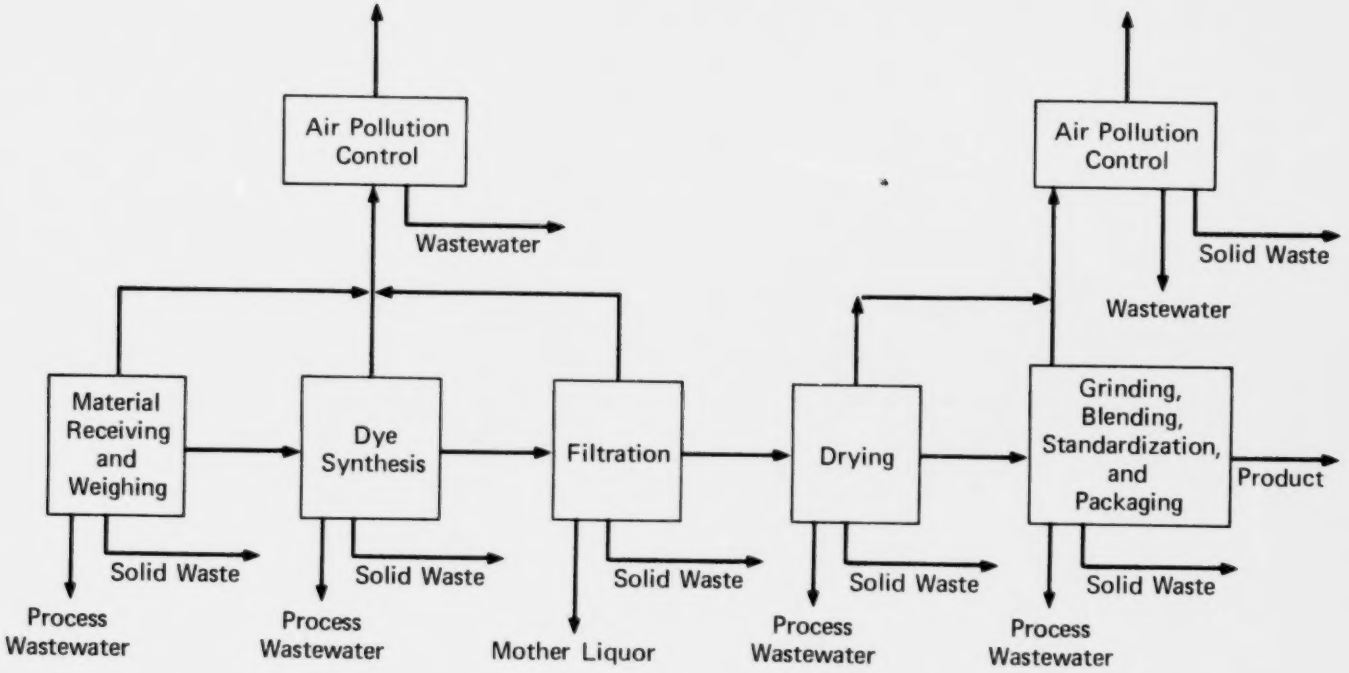

FIGURE 1 PRODUCTION OPERATIONS THAT ARE SOURCES OF WASTE EMISSSIONS IN DYE AND PIGMENT MANUFACTURE

Often sodium chloride or Glauber's salt (sodium sulfate) is added to the blender to reduce the dye concentration to a standard strength (so-called standardization). The amount of salt added to a dye depends on the dye and the producer and may even vary among dye batches at a single facility. Various estimates of the percentage of inert salt in the final marketed dye product are as follows:

<75%	(Industry source)*
50%-92%	(Steadman et al., 1977)
50%	(Shreeve, 1977)
40%-65%	(DETO, 1980)

An inert salt level of 50% has been assumed in the discussion that follows. (An estimate of the salt content of the final product is necessary in discussing actual waste amounts produced by dye manufacturers because the only available production data are for the standardized dye.)

Pigments, which are insoluble, are handled slightly differently; 45% of all pigments are dried, ground, and sold without dilution (Lapp et al., 1979). Another 40% are flushed (dispersed into an oil phase). Based on information from Steadman (1977), we have assumed that flushing adds 65% inert ingredients. The remaining 15% of all pigments are sold as wet filter press cake without processing. This means that, on the average, 27.5% of the final product sold is inert ingredients; i.e., (45% x 0% inert salt) + (40% x 65% oil) + (15% x 10% water in press cake) = 27.5% inert ingredients.

The mother liquor (remaining after filtering out the dye or pigment product) and other process wastewater are treated by processes such as sedimentation and activated sludge to remove residual dyes and other organic compounds by some dye manufacturers before discharge. Other dye manufacturers discharge these wastes directly to municipal sewer systems so that treatment occurs at a publicly owned treatment works.

*Personal communication, S. Gerber, American Cyanamid Co., September 8, 1980.

RAW MATERIAL RECEIVING AND HANDLING

Dye intermediates are received either from other chemical manufacturing sites or from manufacturing operations at the dye manufacturing site. The physical properties of the chemical intermediates for which data were found (see Table 3) indicate that they are almost all solids at ambient temperatures. The intermediates for which no data were found were assumed to be solids also because they are chemically similar to the other intermediates and often of higher molecular weight. Therefore, material from other manufacturing sites is likely to arrive in fiber drums or paper bags. Material from the same site may arrive the same way or in some container such as a tote box designed for transfer and temporary storage of solids. The intermediates are weighed and transferred into the appropriate vessels in the dye reactor train.

Solid Residues

Most solid residues from material receiving will be shipping containers contaminated by chemicals that stick to the walls or fill cracks and crevides. It was estimated that 0.1% of such solids remains in the shipping container. Very few data are available to indicate the disposition of this material. One industry contact* stated that the Atlantic Chemical Corporation, which manufacturers dyes and pigments based on benzidine congeners, sends about one truckload of fiber drums and paper waste to a dump every day. Any chemicals remaining in the drums or on the paper would end up at the dump site. (Manufacturing operations that receive material in temporary storage and transportation containers from their own chemical manufacturing operation may wash out the containers and return them to duty so any chemicals remaining in the container would then go into the process wastewater treatment system; see below.)

To indicate the order of magnitude of the potential solid residue disposal required by dye and pigment manufacturing, it has been assumed that all intermediates arrive in fiber drums or bags, which are later

*Personal communication with M. B. Bochner, Atlantic Chemical Corp., September 10, 1980.

disposed of in a landfill. Since dyes have been assumed to be 50% inert salts, a 0.1% loss of intermediates on a delivered basis is equivalent to approximately a 0.05% loss on a final product dye basis. Since pigments have been assumed to be 27.5% inert, the corresponding loss is equivalent to 0.072% on a final product pigment basis.

Process Wastewater

The material from spills during transfer operations and residual material in temporary storage and transfer containers may be washed away. The amount of water required and the frequency of cleaning is difficult to quantify, and no quantitative estimates have been made.

Vapor and Dust Losses

Vapor losses during chemical intermediate transferring and weighing operations are expected to be small because most of the chemicals are estimated to have low vapor pressures and be solids at room temperature. The loss of solid material from dusts may occur during handling. The vapors and dusts at the weighing and transfer operations at some facilities will be vented to a scrubber unit (DETO, 1980;Keinath, 1976). In the present study, the vapor and dust losses are not estimated separately, but are included in the estimates of the vapor losses that occur during dye synthesis and product filtering.

DYE SYNTHESIS

Solid Residues

The major solid residue produced during dye synthesis is the discharge from a filter press if one is used to clarify the diazonium salts and other intermediate liquors. An example of this filtering operation was found at the Fabricolor facility. A filter cake from clarifying a liquor containing benzidine tetrazonium salts (Celite and carbon are used to form the cake) is washed with water while closed, and the washings are transferred to the coupling vessel where the next synthesis step will occur. A sodium hypochlorite solution is added

to the filter press to oxidize and bleach any organic material on the filter cake, and the resulting solution is discharged to the process sewer. The filter cake is then removed and transported to a landfill (Keinath, 1976).

The water washing step probably removes some benzidine and water-soluble material from the filter cake, although some may remain adsorbed to the carbon. The materials that remain on this filter cake material after water washings are probably the by-products and the azo decomposition products (e.g., as indicated in the previous discussion of dye chemistry, some of these by-products may be N-nitrosamines). If the washed filter cake were removed without further treatment, it might be considered a hazardous material. The sodium hypochlorite solution that is used to treat the filter cake at Fabricolor probably oxidizes some of the organics but may also produce soluble chlorinated aromatics, some of which may have toxic qualities. However, only a small amount of residual organic material is expected to be sorbed to the cake material at this point.

Occasionally, a clarification step is required after a coupling reaction. If the decontamination procedure for the filter is the same as for the tetrazonium salts (washing, followed by oxidation with hypochlorite), the solid waste produced may have little residual organic content. However, if the hypochlorite oxidation step is not used, the filter cake material may contain insoluble by-products of the coupling reactions, including N-nitrosamines.

The solid residues produced by these filtering operations are expected to be small in volume, and have not been quantified. They should, however, be sampled and chemically analyzed to determine if they represent a significant hazard.

Process Wastewater

Process wastewater is produced when reactors are cleaned between dye syntheses. This clean-up water would contain unreacted intermediates, by-products, and dye. Clean-up may not occur between every synthesis,

however, because practice is sometimes to produce dyes in a light to dark sequence, which would disguise any carryover from uncleaned or incompletely cleaned equipment. Because there was no information on clean-up frequency and no data on the chemical content of clean-up waters, the loss of materials from equipment clean up was not quantified separately but instead included in an overall loss estimate.

Other sources of wastewater from dye synthesis include floor washdown, laundry, worker showers (Keinath, 1976), and blowdown from scrubbers. The amount of material in the combined process wastewater has not been well determined. Very limited sampling of process wastewater at an Allied Chemical Corporation facility producing benzidine dyes and pigments showed 963 ppm benzidine (Keinath, 1976). The process wastewater at the facility was not discharged to the plant sewer until after chemial treatment with nitrous acid. Nitrous acid oxidation was reported to produce the benzidine tetrazonium salt, which decomposes to produce (in acidic medium) phenylphenol, chlorobiphenyl, dihydroxybiphenyl, hydroxychlorobiphenyl, phenol, and biphenylphenol (Keinath, 1976). It is quite probable that the nitrous acid will react with any residual secondary amines present to generate nitrosamines. Little or no residual benzidine has been detected in wastewater treated by nitrous acid (Keinath, 1976).

Lapp's (1979) estimate of 1% loss based on raw materials added to the process was used for the loss of intermediates to the process wastewater. These losses would be in the form of unreacted intermediates, by-products, and dye. Because the final product is assumed to be 50% inert salt for a dye and 27.5% inert ingredients for a pigment, these losses are equivalent to 0.5% and 0.72%, respectively, based on final product. Since the losses could occur before significant reaction had occurred or after completion of the synthesis or anywhere in between, equal weight was given to each type of material. The 1/3 share of these losses assigned to intermediates was divided by four to obtain an estimate for individual intermediates because four is a typical number of intermediates. If nitrous acid treatment is used at many facilities,

this estimated loss is probably an overestimate of the amount of the actual intermediates and by-products released to the process sewer, since chemical changes will occur during treatment. The estimate may be a reasonable estimate of the total amount of organic material, however, because nitrous acid treatment was not reported to completely oxidize organics to CO_2 and water. Because the extent to which all manufacturers chemically treat process wastewaters was not known, chemical treatment was not assumed for the industry. The overall waste emission estimate for the entire dye or pigment manufacturing process is not sensitive to these assumptions because much larger losses occur later in the process.

Vapor Losses

During dye and pigment synthesis, vapor losses are expected to be small because the reaction temperatures are low and because the physical properties of the chemical intermediates for which data were found indicate that they have low vapor pressures even at ambient temperatures. The vapor pressures for intermediates and by-products for which no data were found are assumed to be low also. The single exception is ethyl chloride, which is used in only one dye synthesis for a very minor dye. Losses of ethyl chloride may be high, but were not quantified. Many facilities have vents at process vessels that lead to a scrubbing system (Keinath, 1979; DETO, 1980) which should limit releases to the environment. Any vapor losses were not quantified separately but were combined with the vapor losses during materials handling and filtration.

PRODUCT FILTRATION

Solid Residues

The solid residues produced during product filtration are precipitated dye or insoluble pigment that are spilled during transfer of the press cake to the drying operation or remain as a residual in the filter press. In keeping with the estimates of Lapp (1979), total losses of dye or pigment are assumed to be 1% of the organic dye or pigment, which converts to 0.5% and 0.75% on a final standardized product basis for

dyes and pigments, respectively. These solid residue materials are assumed to be washed into the process wastewater system so that product filtration does not produce a solid residue directly, although solid residue may result from wastewater treatment.

Process Wastewater

The major contributors to potential discharges of material from filtration operations are the mother liquor and process wastewater from equipment washwaters. The mother liquor will contain unreacted intermediates, terminated coupling products, other by-products (see Section 3), and dye. To calculate the amounts of these materials that might be present, it was assumed that 5% excess of each coupling component, with respect to benzidine (or its congener), is used during dye or pigment manufacturing. Two percent of the reactants in each coupling step are assumed to go to by-products, with terminated couplings the dominant species.

The extent of precipitation and efficiency of filtration will determine the amount of dye remaining in the mother liquor. We have assumed that 2% of the dye (standardized dye product basis) remains in the mother liquor. This is equivalent to the estimates of 1%-3% made by Lapp (1979). Since pigments are insoluble in water, it has been assumed that no pigment remains in the mother liquor.

The average dye or pigment batch produces 2,000 kg of filter cake, 4,000 kg of final product, and 20,000 liters of mother liquor. These averages were developed from the BIOS (1945) recipes. The following amounts of unreacted intermediate and by-products are estimated to occur (The details of the estimation procedure are shown in Appendix B):

	Concentration in Mother Liquor (ppm)	% of Final Standardized Product
Dye Manufacture		
Each unreacted intermediate (except benzidine and its congeners)	1,500	0.75%
By-products	5,000	2.5
Pigment Manufacture		
Each unreacted intermediate (except benzidine congeners)	2,000	1.0
By-products	7,000	3.5

It is possible that many of the by-products will be insoluble and could precipitate along with the product dye or pigment and that some unreacted intermediates will also salt out when product dyes are precipitated. This means that substantial amounts of these materials could be sold along with the product. (Appendix B shows that as much as 10% of the final product could be unreacted intermediates and by-products if they were precipitated from the mother liquor.) However, because no information was found to confirm this level of contamination, it was assumed that all unreacted intermediates and by-products remained soluble in the mother liquor. There is some justification for this assumption since we have assumed that on a final standardized product basis, 2% of the final dye product remains in solution in the mother liquor. This 2% represents a 4000 ppm concentration of the organic dye molecule which is probably the most insoluble material present. The level of intermediates and by-products in the final product would then be due only to the residual mother liquor remaining in the filter cake before it was dried.

Abrahart (1968) indicates that the residual water content is 10% (200 kg) or 1% of the total mother liquor. If each intermediate were present at 1,500 ppm in the mother liquor, the residual water in the filter cake would contain 1,500 ppm x 200 kg = 0.3 kg of each intermediate. In the final standardized product dye, this 0.3 kg would be 0.3/4,000 = 75 ppm for each intermediate. In a similar manner, the 5,000 ppm by-products in the mother liquor would result in 250 ppm of by-product in the final dye product. The final dye or pigment could thus contain a total of several hundred parts per million of unreacted intermediates and by-products.

Vapor Losses

Vapor losses during filtration would consist primarily of unreacted intermediates because the dye or pigment product and most of the by-products would not have significant vapor pressures. Because almost all the intermediates are also assumed to have low vapor pressures, total vapor losses are estimated to be minimal. Many facilities have dust and vapor control systems that collect the material lost from materials handling, dye synthesis, and the filtration process (DETO, 1980; Keinath, 1976) and process it through a scrubber. Lapp (1979) estimated that the total losses of benzidine and its congeners to the scrubber system from materials handling, dye synthesis, and filtration was 0.25% of the amount added. It would be reasonable to assume the same level of losses for each intermediate used.

Using Direct Green 1 (see Appendix A for details of its production) as a model for all dyes and pigments, one can see that on the average each intermediate represents approximately 10% of the final standardized dye product, so that the 0.25% loss of an ingredient can be expressed as 0.03% on a final dye product basis. For pigments, this figure is 0.04%. If a plant did not have a scrubber system, dusts and vapors could severely contaminate the work place environment before they were washed into the plant wastewater systems or released to the outside environment.

DRYING, GRINDING, STANDARDIZATION, BLENDING, AND PACKAGING

Solid Residues

Solid residues from the final processing or finishing of dyes and pigments would consist principally of dusts produced during drying, grinding, standardization, blending, and packaging. Most of these dusts will be captured by moving air in a vent or hood system when they are used and would then be removed from the air in a baghouse. Boeniger (1980) details the hood system at two facilities manufacturing dyes and pigments based on benzidine and its congeners. Although the hood systems were not adequate to prevent significant exposure to workers,

they did collect most of the dust. Some of the collected dust in pigment processing was returned to the product.

Lapp (1979) estimated that 1%-5% of the organic dye is lost during finishing. This can be expressed as 0.5%-2.5% of the final standardized dye product, and it has been assumed that 2% is typical. This material will be mostly dust collected in the baghouse at facilities that have good engineering controls.

For dry process pigments, Lapp (1979) has estimated that 1%-3% of the final product is lost during drying and grinding. We will assume 3% is lost to cover additional losses during standardization and blending. For pigments that are flushed, losses were estimated by Lapp to be 1%-3%, mostly during transfers between equipment and containers. To be conservative, we will assume 3%. For pigment sold as press cake, losses of product were estimated to be 1%, mostly from material transfers. Most of these pigment losses will probably become solid residues that are either collected in the baghouse facilities or swept up off the floor. The average solid waste production is 2.1% of the final pigment product, computed as follows:

(45% dry processed pigment x 3% loss) + (40% flushed pigment x 3% loss) x (50% inert) + (15% press cake x 1% loss) = 2.1%.

These dye and pigment solid residues have previously been estimated to contain about 75 ppm of each unreacted intermediate other than benzidine and its congeners. They will also contain low levels of benzidine or its congeners. Boeniger (1980) measured benzidine levels in a number of domestically produced dyes and found concentrations less than 20 ppm in the finished product. The levels of the benzidine congeners in finished products currently produced is unknown.

Vapor Losses

There are two potential vapor emission sources in dye and pigment finishing. The drying operations, which removes the 10% mother liquor in the filter press cake, could also volatilize some of the unreacted intermediates and by-products present. With the exception of a few

intermediates such as aniline and ethyl chloride, these materials are known or assumed to have vapor pressures far less than that of water. Therefore, significant volatilization of intermediates, if they were present on the dye or pigment would not be expected during drying. The vapors from product drying will be passed through a baghouse at most facilities but very little condensation and removal of volatilized material is expected there even if significant cooling occurs because the large air flows will prevent vapor saturation. The second opportunity for unreacted intermediates to volatilize occurs if materials are carried from process to process in open tote boxes. However, very little volatilization is expected because of the low temperatures. Some of the organic vapors from open tote boxes will be entrained in air entering scrubbers or baghouses operated to control emissions at specific processing steps. If processed by a scrubber, the vapors will be collected and contribute to contamination of the process wastewater. If processed through a baghouse, the vapors will probably escape to the atmosphere.

SUMMARY OF AQUEOUS WASTE AND SOLID RESIDUE DISCHARGE ESTIMATES

The estimated amounts of intermediates, by-products, and dye or pigment that are discharged by the various operations used in dye and pigment manufacturing are summarized in Table 5 for dyes and Table 6 for pigments. As was discussed in detail previously, these estimates are assumed to be either typical or worst case for the industry and have not taken into account site-specific factors such as the absence or presence of scrubbers on process vessel vents at a particular site. They do not include specific dye or pigment chemistry that might require more or less excess ingredients than assumed or yield more or less by-product; the material estimated to be present in the aqueous stream is subject to wastewater treatment which is discussed below.

Table 5

SUMMARY OF THE ESTIMATED AQUEOUS WASTES AND SOLID RESIDUES PRODUCED BY DYE MANUFACTURING OPERATIONS

(All Losses are Reported as a Percentage of the Weight of the Final Marketed Product that has been Standardized by the Addition of Inert Salts)

Process Step or Operation	Aqueous Wastes				Solid Residues			
	Dye	Benzidine and Congeners	Other Intermediates (each one)	By-product	Dye	Benzidine and Congeners	Other Intermediates (each one)	By-product
Raw material handling	–	a	a	–	–	0.05%[b]	0.05%[b]	–
Synthesis[c]	0.16%	0.04%	0.04%	0.16%	–	–	–	–
Product filtration[d]	2.5	–	0.75	2.5	–	–	–	–
Air Pollution Control[e]	–	0.03	0.03	–	–	–	–	–
Product finishing[f]	–	–	–	–	2	–	–	–
Total	2.66%	0.07%	0.82%	2.66%	2%	0.05%	0.05%	0%

[a] Losses were not quantified separately but are included in Air Pollution Control.

[b] Intermediate residue on fiber drums and shipping containers.

[c] Material in wash down of equipment and floors, laundry, and worker showers.

[d] Material in mother liquor and process wastewaters from washdown of the filter press.

[e] Scrubber treating vents and hoods associated with raw material handling, synthesis, and product filtration.

[f] Dusts from drying and grinding collected in a baghouse.

Table 6

SUMMARY OF THE ESTIMATED AQUEOUS WASTES AND SOLID RESIDUES PRODUCED BY PIGMENT MANUFACTURING OPERATIONS

(All Losses are Reported as a Percentage of the Weight of the Final Marketed Product that Includes Inert Ingredients such as Oil and Filler)

Process Step	Aqueous Wastes				Solid Residues			
	Pigment	Benzidine and Congeners	Other Intermediates (each one)	By-products	Pigment	Benzidine and Congeners	Other Intermediates (each one)	By-products
Raw materials handling	-	a	a	-	-	0.075%[b]	0.075%[b]	-
Synthesis[c]	0.24%	0.06%	0.06%	0.24%	-	-	-	-
Product filtration[d]	0.75	-	1.0	3.5	-	-	-	-
Vent scrubbing[e]	-	0.04	0.04	-	-	-	-	-
Product finishing[f] (including baghouse)	-	-	-	-	2.1	-	-	-
Total	0.99%	0.10%	1.1%	3.74%	2.1%	0.075%	0.075%	0%

[a] Losses were not quantified separately but are included in Air Pollution Control.

[b] Intermediate residue on fiber drums and shipping containers.

[c] Material from washdown of equipment and floors, laundry, and worker showers. Pigment present will probably be suspended rather than dissolved.

[d] Material in the mother liquor and process wastewater from washdown of the filter press. Pigment present will probably be suspended rather than dissolved.

[e] Scrubber treating vents and hoods associated with raw material handling, synthesis, and product filtration.

[f] Dusts from drying and grinding collected in a baghouse.

WASTEWATER TREATMENT

The principal potential source of dye, by-product, or intermediate release to the environment from dye manufacturing operations is the aqueous process wastewater stream. Each dye producer may have a different wastewater treatment system. As has been discussed previously, some producers use chemical reactions (treatment with nitrous acid) to oxidize the organic compounds in process water generated by equipment washdown, air pollution control scrubbers, worker showers, and laundry preceding discharge of material into the plant sewer (Keinath, 1976). Other producers sewer all process wastewaters directly and may discharge to publicly owned treatment works.

Some producers have onsite wastewater treatment plants involving primary, secondary, and tertiary treatment. These treatment plants will all be site-specific designs with site-specific behavior. Games (1977), for example, has reported plant discharge after secondary treatment of 2,200 kg of organics daily from a South Carolina dye manufacturer using one million liters per day of process water. The waste before treatment had a chemical oxygen demand (COD) of about 670 ppm. Treatment plant performance averaged about 70% and 80% reduction of COD and biological oxygen demand (BOD) to produce an effluent with a COD of 200 mg/liter and a BOD of 60 mg/liter. The plant wastewater treatment system consisted of an equalization pond, a neutralization step, an aerated lagoon with a retention time of less than 5 days, and two large settling ponds with a retention time of 19 days.

Anliker (1979) has reported an effluent concentration before treatment from a dyestuff manufacture as 900-4,000 ppm BOD and 600-1,000 ppm total organic carbon (TOC). Other documents (such as EPA, 1975) give wastewater flows at six different dye manufacturing plants as 33, 114, 175, 200, 800, and 1,800 liters/kg finished product. Sampling of these wastestreams gave the following ranges: 200-5,000 ppm BOD, 1,200-4,000 ppm COD, and 500-2,000 ppm TOC.

Keinath (1976) reports that typical wastewater flows (including mother liquor) are 250-750 liters/kg finished product. Based on the

aqueous emission levels indicated in Tables 5 and 6, these wastewater flows might have 10-30 ppm of each unreacted intermediate (except benzidine and its congeners) and 30-100 ppm of by-products. For example, manufacture of 1 kg of standardized dye is estimated to release to the process sewer 0.0266 kg of by-products. In 250 liters of water, this material would have a concentration of 106 mg/liter. Benzidine and congener concentrations will be lower and in the range of 1-3 ppm. These predicted benzidine concentrations are higher than the 1 to 100 ppb benzidine levels reported for facilities where nitrous acid treatment was used for process wastewater from equipment washdown and scrubbers (Keinath, 1976). Nitrous acid treatment of selected process wastewaters can almost eliminate aqueous discharges of benzidine and its congeners. Oxidation of the mother liquor would be required to significantly reduce aqueous discharges of unreacted intermediates and by-products.

A complete assessment of emissions to all media (air, water, solid residue) would have to consider each manufacturer's plant individually in terms of plant operation, wastewater treatment plant operation, and the specific dyes produced. This is beyond the scope of the current study, which necessarily must neglect site-specific factors. Consequently, the behavior of the organics that might be present in wastewaters will be discussed with respect to potential wastewater treatment operations. Attention will focus on biological treatment processes because these will be present either at most manufacturing sites or at the municipal wastewater treatment systems receiving the wastewater from the manufacturing site.

The behavior of the organic materials during wastewater treatment is discussed in terms of the following four classes of material thought to be present:

(1) Benzidine and its congeners
(2) Unreacted intermediates other than benzidine and its congeners
(3) Product dye
(4) Reaction by-products.

Benzidine and Congeners

There is good evidence that benzidine, o-tolidine, and o-dianisidine are degraded under acclimated aerobic treatment and that little of these materials will be adsorbed on the biological sludge produced during treatment (Tabak and Barth, 1978; Baird et al., 1977; Meyer et al., 1979; Barth and Bunch, 1979). 3,3'-Dichlorobenzidine may adsorb extensively to a variety of sediments (Sikka et al., 1978), but no biodegradability information was found. The types of oxidation products of benzidine produced in aerobic treatment systems are 4,4'-dihydroxybiphenyl, 4-hydroxy-4'-aminobiphenyl, aniline, phenol, and pyrocatechol (Barth and Bunch, 1979) and substituted quinones (Kirk-Othmer, 1978).

Keinath (1976) has suggested that 90% of benzidine is degraded and 10% is adsorbed to treatment sludge. However, for this assessment we have assumed no oxidation would occur either at the manufacturer's treatment plant or at a POTW receiving untreated effluent because discharges will be episodic and not allow acclimated cultures to develop.

Under certain circumstances, a sludge with high levels of benzidine can be produced. Keinath (1976) has reported that one dye manufacturer used a lime precipitation primary treatment process which produced a sludge containing 2 ppm benzidine whereas the water contained only parts per billion. The sludge may also contain dye and degradation products.

Unreacted Intermediates Other Than Benzidine and its Congeners

Physical property data and biotreatability information were found for only a few intermediates. What data there were showed moderate to high solubility in water and weak adsorption to organic material (low K_{OC}). Therefore, it seems reasonable to assume that these materials will not partition strongly onto sludge during wastewater treatment. Some compounds such as phenol are readily biodegradable in adapted systems. Some of the sulfonated aromatics are resistant to degradation (Meyer et al., 1979). In the present study, biodegradation was assumed not to occur because the episodic nature of discharges that result from the batch nature of dye manufacture does not permit an adapted culture to develop.

Product Dye

The sources of information on biodegradation of dyes* indicated that biodegradation of dyes and pigments does not occur to a significant extent in aerobic wastewater treatment processes. In particular, biotreatment systems were not found to acclimate to dyes (ADMI, 1973), and some systems may be inhibited by dyes (ADMI, 1973). The pigments are, in general, not readily biodegradable in aerobic systems (Anliker and Clarke, 1979). Several of these studies also indicate that, at sludge concentrations typical of wastewater treatment facilities, adsorption would not be significant except for some direct dyes which have an affinity for sludge in biotreatment processes.

Reaction By-Products

Only a few of the many by-products possible based on theoretical chemistry have been identified by actual chemical analysis. As was discussed in Section 3 on dye chemistry, benzidine and its congeners are only partially coupled to the other intermediates, with the uncoupled diazonium group being replaced by a hydroxide or chloride. The by-products of more complex dyes will include these types of compounds plus some coupled products not derived from benzidine or its congeners (resulting from coupling of diazonium salts made from other aromatic amines). N-nitrosamines may be present in the process wastewater.

Little information was found on the physical or biological properties of these compounds, so it is difficult to determine how wastewater treatment would affect them. Substantial rates of biodegradation are not expected. Meyer et al. (1979) found that, under aerobic conditions, the biodegradation rate of derivatives of the simple azo compound, phenylazonaphthalene, was affected by the nature of the substituents (e.g., SO_3H, and COOH) present. Double substitution was found to

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*ADMI (1973), Keinath (1976), DETO (1980), Hitz et al. 1978), Dieckhues (1961), Tincher (1978), Baird et al. (1977), Porter (1973), Dubin and Wright (1975), Tabak and Barth (1978), Uroshigawa and Yonezawa (1977), Kappeler et al. (1978), Flege (1970), Idaka et al. (1978), Meyer et al., 1979).

inhibit the degradation and, whenever a sulfonic acid group was present, the degradation was significantly reduced in all cases studied.

For this assessment, we have assumed that by-products are only slowly biodegraded and not strongly adsorbed to sediment or biological material. Studies have shown that the dyes themselves are not strongly sorbed under the conditions of wastewater treatment, so related but smaller molecules are not likely to be either.

Summary of Results of Wastewater Treatment

The previous discussion has shown that the behavior of dye intermediate, by-products, and dye is incompletely understood with respect to biodegradability and sorption onto solids. In addition, even compounds that are biodegradable may not be degraded in a wastewater treatment system because of the episodic nature of discharges due to the batch production of dyes. The interval between batches may be long enough for the bacteria in the system to lose the ability to degrade a particular compound. Compounds may also be present that interfere with biodegradation. We have assumed that biological wastewater treatment is ineffective to deal with this uncertainty as to treatability of dye plant aqueous wastes. Consequently, all material released to process sewers is assumed to be released to the environment. Furthermore, although it is recognized that some components in the wastewater are more likely to be found on the solids produced by treatment than in the aqueous phase, all material emissions are considered to be in a joint aqueous-solid phase. This assignment actually reflects the expectation that every chemical in process wastewater will be found at some concentration in both the solid and aqueous phases produced by wastewater treatment.

Section 6

SOLID RESIDUE AND AQUEOUS WASTE PRODUCTION

The amounts of solid residues and aqueous wastes produced by dye and pigment manufacture were estimated for each dye and pigment during the engineering analysis developed in Section 5. For this analysis, "solid residue" includes only the identifiable solid residue associated with shipping container disposal and dye or pigment fines collected in baghouses. The "aqueous waste" is the estimated amount of material in dye or pigment plant process wastewater before the final wastewater treatment system. Wastewater treatment, which may take place at the manufacturing site or a municipal wastewater treatment system, is assumed to involve sedimentation followed by biological treatment and final clarification. These treatments are assumed to be ineffective in reducing the amount of each compound by any degradation, but will partition the material between wastewater treatment solids and the aqueous effluent. The wastewater treatment solids will probably be landfilled and the effluent discharged to surface waters. Because it was impossible to predict what the partitioning of intermediates between the wastewater treatment solids and the aqueous effluent would be, each aqueous emission should be considered as a joint "aqueous-solid waste" stream.

It is important to realize that dye and by-products may be on the wastewater treatment solids because landfilling will place them in an anaerobic environment where reductive reactions can take place. Diekhues (1961) found, for a variety of dyes, that reductive splitting of the azo linkage occurred. This means that benzidine and its congeners, as well as the other dye intermediates, could be released in a landfill even from dye wastes that did not originally contain these materials in a free state.

Table 7 summarizes the estimated emissions of intermediates and by-products for dyes and pigments where the intermediates could be identified

from information in Colour Index. For the dyes and pigments without C.I. numbers, only the emissions of benzidine and its congeners could be estimated because the other intermediates are not identified. The mass emission of the unknown intermediates and by-products was estimated by analogy to the dyes and pigments with known ingredients. The dyes and pigments in the table are grouped by dye use category (direct, acid, pigment, azoic) and within each use category by the particular benzidine congener used as the basis for the dye or pigment. Then the dyes and pigments are listed in the order of their production volume. Letter codes (defined in Table 8) indicate the producers for each dye or pigment.

The amount in the solid or aqueous waste stream of each of the intermediates used was obtained by multiplying the dye or pigment production value from Table 1 by the emission factors in Table 5 or Table 6. As an example, for Direct Black 38, which is the first dye in Table 7, the solid residue due to materials handling of each intermediate was obtained by multiplying the production value of 373 metric tons/yr for the standardized dye product by the emission factor 0.05% to obtain the estimate of 186 kg/yr. For dyes and pigments where production levels were reported in public sources only as greater than some lower limit, the lower limit was used because there was no way to estimate the actual amount produced. The waste emissions listed for benzidine for all of the dyes and pigments based on benzidine should probably be considered as a special case. Boeniger (1980) reports that the U.S. facility producing benzidine-based dyes and pigments actually uses purchased hydrazobenzene as a starting material. Thus, the estimated solid residue emissions which are due solely to material handling, are probably actually the purchased hydrazobenzene. The hydrazobenzene is converted to benzidine in the tetrazotization reactor, so all other emissions listed for the aqueous stream are probably benzidine.

When all of the intermediates required for a dye were not known, we used an emission factor of 0.15% (which assumes three intermediates besides benzidine and its congeners) to estimate total solid

emissions of intermediates other than benzidine and its congeners. Total aqueous-solid emissions of the unknown intermediates were estimated with an emission factor of 2.46%, which is 3 times the single intermediate emission factor. Azoic compounds were treated the same way as dyes.

The copper required for two o-dianisidine based dyes and the p-toluene sulfonyl chloride used in the production of three acid dyes do not become part of the dye molecule via an azo linkage. For the copper, because the chemistry of its reactions with o-dianisidine could not be studied within the scope of the task, no excess reactant was assumed and the only significant losses were assumed to be the solid residues from materials handling. Since copper has a much lower molecular weight than the organic intermediates, the materials handling loss emission factor of 0.05% of final standardized dye production probably overestimates the actual amount of copper in solid wastes. This may compensate for the fact that aqueous losses due to excess copper reactant have not been calculated. For the p-toluene sulfonyl chloride, because the dyes involved are relatively minor, this chemical was treated the same as other intermediates even though, in practice, different kinds of by-products would be formed.

Table 8 gives the full names of the producers associated with the letter codes used in Table 7, and Table 9 lists the dyes and pigments based on benzidine and its congeners that they make. The identity and corporate ownership of the producers is based on 1978 information. Since then, several dye production facilities or dye lines were sold. Sales that were announced in trade journals are shown as footnotes in Table 8. A systematic search was not made to verify that all such sales have been listed, so the table may not be complete.

The estimated discharges of each intermediate from specific dye and pigment manufacturing were summed to indicate the total amount, on an industry-wide basis, of each intermediate estimated to be in solid residue and in the aqueous waste streams. These industry-wide emission estimates are shown in Table 10, listed in the order of the amount estimated to be in the solid waste stream (because solid wastes are the primary focus of this study). These industry-wide estimates could over-

state the emissions of some intermediates if industry practice is different from the assumptions developed in the engineering analysis. They also probably understate the emissions for the intermediates used in dyes and pigments where only the lower production limit was known. It is possible that if actual production values were known for these dyes and pigments and used to estimate emissions, some of the intermediate emissions now judged to be minor relative to the top ten could become more important. Two of the benzidine congeners (3,3'-dichlorobenzidine and o-dianisidine) and hydrazobenzene (which is the source of benzidine) are among the compounds estimated to represent the ten largest emissions. Benzidine is listed directly after hydrazo-benzene because it is directly associated with the same dyes that are estimated to release hydrazobenzene-containing solid wastes. The three compounds that are estimated to account for the bulk of all emissions, 3,3'-dichloro-benzidine, acetoacetanilide, and o-acetoacetotoluidide, are all associated with pigment production.

Based on the estimates in Table 10, the industry-wide total amount of identified intermediates in the solid waste from the manufacture of dyes and pigments based on benzidine and its congeners is 14.6 MT/yr. The total amount of dye or pigment in the solid residue (obtained by summing the values for each dye and pigment in Table 7) is estimated to be 203 MT/yr, which makes the dye and pigments themselves the more significant synthetic organic component of the total solid residue stream. The total amount, industry-wide, of intermediates estimated to be in the aqueous waste is 127 MT/yr. This aqueous waste is also estimated to contain 125 MT/yr of dye and pigment and 347 MT/yr of reaction by-products. It is interesting to note that if only 10% of the intermediates estimated to be in the aqueous stream were actually adsorbed on wastewater treatment solids, then the amount of intermediates estimated to be in the solid residue from dye and pigment manufacture would almost double. In a similar manner, if only 10% of the by-products were to be adsorbed on wastewater treatment solids, then these by-products would be a significant fraction of the synthetic organic chemicals contained in the solid residue stream.

Table 7

ESTIMATED WASTES PRODUCED IN MANUFACTURING DYES AND PIGMENTS BASED ON BENZIDINE AND ITS CONGENERS

Producers	Product C.I. No.	Product Name	Annual Production (metric tons/yr)	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Aqueous Waste
Benzidine-Based Direct Dyes						
FAB	30235	Direct black 38	373	Direct black 38	7460	9922
				Aniline	186	3059
				1-Amino-8-hydroxy-3,6-naphthalene disulfonic acid	186	3059
				Hydrazobenzene	186	-
				Benzidine	-	261
				m-Phenylenediamine	186	3059
				By-products	-	9922
FAB	22590	Direct blue 2	99	Direct blue 2	1980	2633
				1-Amino-8-hydroxy-3,6-naphthalene disulfonic acid	50	812
				6-Amino-4-hydroxy-2-naphthalene sulfonic acid	50	812
				Hydrazobenzene	50	-
				Benzidine	-	69
				By-products	-	2633
FAB	30295	Direct green 6	49	Direct green 6	980	1303
				1-Amino-8-hydroxy-3,6-naphthalene disulfonic acid	25	402
				Phenol	25	402
				Hydrazobenzene	25	-
				Benzidine	-	34
				p-Nitroaniline	25	402
				By-products	-	1303

Table 7

ESTIMATED WASTES PRODUCED IN MANUFACTURING DYES AND PIGMENTS BASED ON BENZIDINE AND ITS CONGENERS

Producers	Product C.I. No.	Product Name	Annual Production (metric tons/yr)	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Aqueous Waste
FAB	--	Resin F. Black WP	38	Resin F. Black WP	760	1011
				Hydrazobenzene	19	-
				Benzidine	-	27
				Unknown intermediates*	57	935
				By-products	-	1011
FAB	30145	Direct brown 95	34	Direct brown 95	680	904
				Salicylic acid	17	279
				2-Amino-1-phenol-4-sulfonic acid	17	279
				Resorcinol	17	279
				Hydrazobenzene	17	-
				Benzidine	-	24
				By-products	-	904
FAB	30120	Direct brown 154	29	Direct brown 154	580	771
				Sulfanilic acid	15	238
				Toluene-2,4-diamine	15	238
				Hydrazobenzene	15	-
				Benzidine	-	20
				2,3-Cresotic acid	15	238
				By-products	-	771

*Dye was assumed to require 3 intermediates in addition to benzidine.

Table 7

ESTIMATED WASTES PRODUCED IN MANUFACTURING DYES AND PIGMENTS BASED ON BENZIDINE AND ITS CONGENERS

Producers	Product C.I. No.	Product Name	Annual Production (metric tons/yr)	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Aqueous Waste
FAB	22610	Direct blue 6	28	Direct blue 6	560	748
				Hydrazobenzene	14	-
				Benzidine	-	20
				1-Amino-8-hydroxy-3-6-naphthalene disulfonic acid	14	230
				By-products	-	748
FAB	35660	Direct brown 31	17	Direct brown 31	340	452
				Hydrazobenzene	9	-
				Benzidine	-	12
				o-Phenylsulfonyl-2R acid	9	139
				Toluene-2,4-diamine	9	139
				Salicylic acid	9	139
				Naphthionic acid	9	139
				By-products	-	452
FAB	22120	Direct red 28	17	Direct red 28	340	452
				Hydrazobenzene	9	-
				Benzidine	9	12
				Naphthionic acid	9	139
				By-products	-	452

Table 7

ESTIMATED WASTES PRODUCED IN MANUFACTURING DYES AND PIGMENTS BASED ON BENZIDINE AND ITS CONGENERS

Producers	Product C.I. No.	Product Name	Annual Production (metric tons/yr)	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Aqueous Waste
FAB	36300	Direct brown 74	15	Direct brown 74	300	399
				Hydrazobenzene	8	-
				Benzidine	-	11
				1,6(and 1,7)-Cleve's acid	8	123
				Salicylic acid	8	123
				Phenol	8	123
				4,8-Diamino-2,6-naphthalene disulphonic acid	8	123
				By-products	-	399
FAB	22311	Direct brown 2	13	Direct brown 2	260	346
				6-Amino-4-hydroxy-2-naphthalene sulfonic acid	7	107
				Hydrazobenzene	7	-
				Benzidine	-	9
				Salicylic acid	7	107
				By-products	-	346
FAB	22130	Direct orange 8	12	Direct orange 8	240	319
				Salicylic acid	6	98
				Naphthionic acid	6	98
				Hydrazobenzene	6	-
				Benzidine	0	8
				By-products	-	319

Table 7

ESTIMATED WASTES PRODUCED IN MANUFACTURING DYES AND PIGMENTS BASED ON BENZIDINE AND ITS CONGENERS

Producers	Product C.I. No.	Product Name	Annual Production (metric tons/yr)	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Aqueous Waste
FAB	30245	Direct black 4	12	Direct black 4	240	319
				Aniline	6	98
				1-Amino-8-hydroxy-3,6, naphthalene disulphonic acid	6	98
				Hydrazobenzene	6	-
				Benzidine	-	8
				Toluene-2,4-diamine	6	98
				By-products	-	319
FAB	22310	Direct red 1	12	Direct red 1	240	319
				6-Amino-4-hydroxy-2- naphthalene sulfonic acid	6	98
				Salicylic acid	6	98
				Hydrazobenzene	6	-
				Benzidine	-	8
				By-products	-	319
FAB	30280	Direct green 1	6	Direct green 1	120	160
				Aniline	3	49
				1-Amino-8-hydroxy-3,6- naphthalene disulfonic acid	3	49
				Hydrazobenzene	3	-
				Benzidine	-	3
				Phenol	3	49
				By-products	-	160

Table 7

ESTIMATED WASTES PRODUCED IN MANUFACTURING DYES AND PIGMENTS BASED ON BENZIDINE AND ITS CONGENERS

Producers	Product C.I. No.	Product Name	Annual Production (metric tons/yr)	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Aqueous Waste
FAB	30140	Direct brown 6	4	Direct brown 6	80	106
				Sulfanilic acid	2	33
				Resorcinol	2	33
				Hydrazobenzene	2	-
				Benzidine	-	3
				Salicylic acid	2	33
				By-products	-	106
ortho-Dianisidine-Based Direct Dyes						
ALT ATL BAS DUP GAF TRC	24401	Direct blue 218	445	Direct blue 218	8900	11837
				1-Amino-8-hydroxy-3,6-naphthalene disulfonic acid	223	3649
				o-Dianisidine	223	311
				Copper*	223	-
				By-products	-	11837
AC ALT ATL BAS GAF FAB TRC	-	Direct blue 80	133	Direct blue 80	2660	3538
				o-Dianisidine	67	93
				Unknown intermediates†	200	3272
				By-products	-	3538

* Copper sulfate and sodium acetate react with the methoxy groups in a special processing step after the dye has been filtered.

† Dye was assumed to require 3 intermediates in addition to o-dianisidine.

Table 7

ESTIMATED WASTES PRODUCED IN MANUFACTURING DYES AND PIGMENTS BASED ON BENZIDINE AND ITS CONGENERS

Producers	Product C.I. No.	Product Name	Annual Production (metric tons/yr)	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Aqueous Waste
ALT ATL BAS FAB GAF TRC	23155	Direct blue 98	123	Direct blue 98	2460	3272
				N-Phenyl-7-amino-4-hydroxy-2-naphthalene sulfonic acid	62	1009
				o-Dianisidine	62	86
				1-Hydroxy-3,8-naphthalene disulfonic acid	62	1009
				By-products	-	3272
AC BAS GAF TRC ATL	24410	Direct blue 1	41	Direct blue 1	820	1091
				4-Amino-5-hydroxy-1,3-naphthalene disulfonic acid	21	336
				o-Dianisidine	21	29
				By-products	-	1091
BAS DUP GAF VPC	24400	Direct blue 15	> 10	Direct blue 15	200	266
				1-Amino-8-hydroxy-3,6-naphthalene disulfonic acid	5	82
				o-Dianisidine	5	7
				By-products	-	266

Table 7

ESTIMATED WASTES PRODUCED IN MANUFACTURING DYES AND PIGMENTS
BASED ON BENZIDINE AND ITS CONGENERS

Producers	Product C.I. No.	Product Name	Annual Production (metric tons/yr)	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Aqueous Waste
ALT TRC VPC	-	Direct blue 160	> 7.5	Direct blue 160	150	200
				o-Dianisidine †	4	5
				Unknown intermediates †	11	185
				By-products	-	200
AC ALT ATL	24411	Direct blue 76	> 5	Direct blue 76	100	133
				4-Amino-5-hydroxy-1,3-naphthalene disulfonic acid	3	41
				o-Dianisidine	3	4
				Copper*	3	-
				By-products	-	133
ATL FAB	-	Direct blue 100	> 5	Direct blue 100	100	133
				o-Dianisidine	3	4
				Unknown intermediates †	9	123
				By-products	-	133

* Copper sulfate and sodium acetate react with the methoxy groups in a special processing step after the dye has been filtered.

† Dye was assumed to require 3 intermediates in addition to o-dianisidine.

Table 7

ESTIMATED WASTES PRODUCED IN MANUFACTURING DYES AND PIGMENTS
BASED ON BENZIDINE AND ITS CONGENERS

Producers	Product C.I. No.	Product Name	Annual Production (metric tons/yr)	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Aqueous Waste
ATL	24140	Direct blue 8	> 2	Direct blue 8	40	53
				o-Dianisidine	1	1
				1-Hydroxy-4-naphthalene sulfonic acid	1	16
				By-products	-	53
ATL	24175	Direct blue 151	> 2	Direct blue 151	40	53
				7-Amino-4-hydroxy-2-naphthalene sulfonic acid	1	16
				o-Dianisidine	1	1
				1-Hydroxy-4-naphthalene sulfonic acid	1	16
				By-products	-	53
ortho-Tolidine-Based Direct Dyes						
AC FAB TRC ATL	23500	Direct red 2	> 9	Direct red 2	180	239
				o-Tolidine	5	6
				Naphthionic acid	5	74
				By-products	-	239

Table 7

ESTIMATED WASTES PRODUCED IN MANUFACTURING DYES AND PIGMENTS
BASED ON BENZIDINE AND ITS CONGENERS

Producers	Product C.I. No.	Product Name	Annual Production (metric tons/yr)	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Aqueous Waste
BAS GAF TRC	23630	Direct red 39	> 7	Direct red 39	140	186
				2-Hydroxy-6,8-naphthalene disulfonic acid	4	57
				o-Tolidine	4	5
				Phenol	4	57
				Ethyl chloride*	4	0†
				By-products	-	186
ATL TRC	23797	Direct blue 25	> 5	Direct blue 25	100	133
				o-Tolidine	3	4
				1,8-Dihydroxy-3,6-naphthalene disulfonic acid	3	41
				By-products	-	133
TRC	23850	Direct blue 14	> 2	Direct blue 14	40	53
				o-Tolidine	1	1
				1-Amino-8-hydroxy3,6-naphthalene disulfonic acid	1	16
				By-products	-	53

*The ethyl chloride reacts under pressure with the hydroxy-group in a special processing step after all coupling reactions are complete. An ethoxy-group results and hydrochloric acid is formed.

†Unreacted ethyl chloride will volatilize from wastewater during treatment.

Table 7

ESTIMATED WASTES PRODUCED IN MANUFACTURING DYES AND PIGMENTS BASED ON BENZIDINE AND ITS CONGENERS

Producers	Product C.I. No.	Product Name	Annual Production (metric tons/yr)	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Aqueous Waste
ATL	-	Direct brown 230	> 2	Direct brown 230	40	53
				o-Tolidine	1	1
				Unknown intermediates*	3	48
				By-products	-	53
ATL	23365	Direct orange 6	> 2	Direct orange 6	40	53
	23375	Direct orange 6		o-Tolidine	1	1
				2,4-Diaminobenzene sulfonic acid	1	16
				2,3-Cresotic acid	1	16
			or	o-Tolidine	1	1
				Salicylic acid	1	16
				4,6-Diamino-m-toluene sulfonic acid	1	16
				By-products	-	53

*Dye was assumed to require 3 intermediates in addition to o-tolidine.

Table 7

ESTIMATED WASTES PRODUCED IN MANUFACTURING DYES AND PIGMENTS BASED ON BENZIDINE AND ITS CONGENERS

Producers	Product C.I. No.	Product Name	Annual Production (metric tons/yr)	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Aqueous Waste
Benzidine-Based Acid Dyes						
FAB	22245	Acid red 85	18	Acid red 85	360	479
				2-Hydroxy-6,8-naphthalene sulfonic acid	9	148
				Phenol	9	148
				Hydrazobenzene	9	-
				Benzidine	-	13
				p-Toluenesulfonyl chloride*	9	148
				By-products	-	479
2,2'-Disulfobenzidine-Based Acid Dyes						
ATL BAS	22890	Acid red 97	> 5	Acid red 97	100	133
				2,2'-Disulfobenzidine	3	4
				2-Naphthol	3	41
				By-products	-	133
AC	22910	Acid yellow 42	> 2	Acid yellow 42	40	53
				2,2'-Disulfobenzidine	1	1
				3-Methyl-1-phenyl-5-pyrazolone	1	16
				By-products	-	53

*This intermediate reacts with the phenolic groups present in the coupled product to form the p-toluene sulfonyl ester.

Table 7

ESTIMATED WASTES PRODUCED IN MANUFACTURING DYES AND PIGMENTS BASED ON BENZIDINE AND ITS CONGENERS

Producers	Product C.I. No.	Product Name	Annual Production (metric tons/yr)	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Aqueous Waste
m-Tolidine-Based Acid Dyes						
VPC	23266	Acid red 111	> 2	Acid red 111	40	53
				1-Hydroxy-3,6-naphthalene disulfonic acid	1	16
				m-Tolidine	1	1
				Phenol	1	16
				p-Toluene sulfonyl chloride*	1	16
				By-products	-	53
o-Tolidine-Based Acid Dyes						
ALT ATL TRC	23635	Acid red 114	140	Acid red 114	2800	3724
				2-Hydroxy-6,8-naphthalene sulfonic acid	70	1148
				o-Tolidine	70	98
				Phenol	70	1148
				p-Toluene sulfonyl chloride*	70	1148
				By-products	-	3724
ATL TRC	-	Acid red 167	> 5	Acid red 167	100	133
				o-Tolidine	3	4
				Unknown intermediates†	9	12?
				By-products	-	133

* This intermediate reacts with the phenolic groups present in the coupled product to form the p-toluene-sulfonyl ester.

† Dye was assumed to require 3 intermediates in addition to o-tolidine.

Table 7

ESTIMATED WASTES PRODUCED IN MANUFACTURING DYES AND PIGMENTS BASED ON BENZIDINE AND ITS CONGENERS

Producers	Product C.I. No.	Product Name	Annual Production (metric tons/yr)	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Aqueous Waste
3,3'-Dichlorobenzene-Based Pigments						
AMS SDH APO ICC BOR HPC GLX HRC IDC HSC ROM HST SNA	21090	Pigment yellow 12	5380	Pigment yellow 12	113000	53000
				3,3'-Dichlorobenzidine	4035	5380
				Acetoacetanilide	4035	59000
				By-products	-	201000
AMS SDH BNS S GAF ROM HPC HRC HSC HSH IDC GLX ICC BUC HST APO SNA	21095	Pigment yellow 14	1420	Pigment yellow 14	30000	14000
				3,3'-Dichlorobenzidine	1065	1420
				o-Acetoacetotoluidide	1065	16000
				By-products	-	53000
AMS HSC BUC HST INP ICC GLX IDC HPC ROM HSH SDH HRC SNA	21105	Pigment yellow 17	621	Pigment yellow 17	13000	6148
				3,3'-Dichlorobenzidine	466	621
				o-Acetoacetanisidide	466	6831
				By-products	-	23000

Table 7

ESTIMATED WASTES PRODUCED IN MANUFACTURING DYES AND PIGMENTS
BASED ON BENZIDINE AND ITS CONGENERS

Producers	Product C.I. No.	Product Name	Annual Production (metric tons/yr)	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Aqueous Waste
SNA HSC APO HST BUC IDC GLX SDH HPC AMS	21100	Pigment yellow 13	232	Pigment yellow 13	4872	2297
				3,3'-Dichlorobenzidine	174	232
				2,4-Acetoacetoxylidide	174	2552
				By-products	-	8677
AMS HSH GLX HPC HRC HSC ICC S KON SNA	21110	Pigment orange 13	108	Pigment orange 13	2268	1069
				3,3'-Dichlorobenzidine	81	108
				3-Methyl-1-phenyl-5-pyrazolone	81	1188
				By-products	-	4039
HRC ROM BUC S GLX SDH IND	21115	Pigment orange 34	38	Pigment orange 34	798	376
				3,3'-Dichlorobenzidine	29	38
				3-Methyl-1-p-tolyl-5-pyrazolone	29	418
				By-products	-	1421
HRC HSH SNA	21120	Pigment red 38	> 7	Pigment red 38	147	69
				3,3'-Dichlorobenzidine	5	7
				3-Carbethoxy-1-phenyl-5-pyrazolone	5	77
				By-products	-	262

Table 7

ESTIMATED WASTES PRODUCED IN MANUFACTURING DYES AND PIGMENTS
BASED ON BENZIDINE AND ITS CONGENERS

Producers	Product C.I. No.	Product Name	Annual Production (metric tons/yr)	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Aqueous Waste
HPC ICC	21096	Pigment yellow 55	> 1	Pigment yellow 55	21	10
				3,3'-Dichlorobenzidine	1	1
				p-Acetoacetotoluidide	1	11
				By-products	-	37
ortho-Dianisidine-Based Pigments						
HPC HRC BNS HSH GLX HST SOH ROM	21160	Pigment orange 16	211	Pigment orange 16	4431	2089
				o-Dianisidine	158	211
				Acetoacetanilide	158	2321
				By-products	-	7891
GLX ICC	21180	Pigment blue 25	>1	Pigment blue 25	21	10
				o-Dianisidine	1	1
				3-Hydroxy-2-naphthanilide	1	11
				By-products	-	37
HRC	21200	Pigment red 41	> 5	Pigment red 41	105	50
				o-Dianisidine	4	5
				3-Methyl-1-phenyl-5-pyrazolone	4	55
				By-products	-	187

Table 7

ESTIMATED WASTES PRODUCED IN MANUFACTURING DYES AND PIGMENTS BASED ON BENZIDINE AND ITS CONGENERS

Producers	Product C.I. No.	Product Name	Annual Production (metric tons/yr)	Material Released to Environment	Quantity Released (kg/yr) Solid Residue	Quantity Released (kg/yr) Aqueous Waste
Azoic Compounds*						
BUC PCW	37575	Azoic coupling component 3	>5	Azoic coupling component 3 o-Dianisidine 3-Hydroxy-2-naphthalene carboxylic acid	100 3 3	133 4 41
ATL	37235	Azoic diazo component 48	>2	o-Dianisidine	-	-
BUC	37610	Azoic coupling component 5	>2	Azoic coupling component 5 o-Tolidine Ethyl acetoacetate Ketene dimer $(CH_2CO)_2$	40 1 1 1	53 1 16 16
ALL BAS BUC GAF	-	Azoic blue composition 3	>10	Azoic blue composition 3 Unknown mixture of an azoic diazo component and azoic coupling component	- -	- -
BUC	-	Azoic black composition 4	>2	Azoic black composition 4 Unknown mixture of an azoic diazo component and azoic coupling component	- -	- -

*By-products are not shown because the chemistry of producing these materials was not studied.

Table 8

DIRECTORY OF DYE AND ORGANIC PIGMENT MANUFACTURERS, 1978

Names of manufacturers that reported production and/or sales of dyes based on benzidine and its congeners to the U.S. International Trade Commission for 1978 are listed below in order of their identification codes as used in Table 7.

Code	Name of Company
Dye Manufacturers	
AC	American Color & Chemical Corp.
ALL	Alliance Chemical Corp.
ALT	Crompton & Knowles Corp., Dyes and Chemical Div.
ATL	Atlantic Chemical Corp.
BAS	BASF Wyandotte Corp.
BUC	Synalloy Corp., Blackman-Uhler Chemical Div.
DUP[a]	E.I. du Pont de Nemours & Co., Inc.
FAB	Fabricolor Incorporated
GAF	GAF Corp.
PCW	Pfister Chemical Works
TRC	Toms River Chemical Corp.
VPC	Mobay Chemical Corp. Verona Dyestuff Div.
Pigment Manufacturers	
AMS	Ridgway Color & Chemicals
APO	Apollo Colors, Inc.
BNS	Binney and Smith, Inc.
BOR	Borden, Inc., Princing Ink Div., Pigments Div.
BUC	Synalloy Corp., Blackman-Uhler Chemical Div.
DUP[a]	E. I. du Pont de Nemours & Co., Inc.
GAF[b]	GAF Corp.
GLX	Galaxie Chemical Corp.
HPC	Hercules, Inc.
HRC	Harmon Colors Corp.
HSC	Chemtron Corp., Pigments Div., Subsid. of Allegheny Ludlum Industries, Inc.
HSH	Harshaw Chemical Co.
HST	American Hoechst Corp. Industrial Chemicals Div.
ICC	Inmont Corp.
IDC	Industrial Color, Inc.
IND	Indol Chemical Co., Inc.
KON	H. Kohnstamm & Co., Inc.
ROM	United Merchants & Manufacturers, Inc. Roma Chemical Div.
S	Sandoz, Inc., Colors & Chemicals Div.
SDH	Sterling Drug, Inc. Hilton Davis Chemical Co. Div.
SNA	Sun Chemical Corp., Pigments Div.
TMS	Sterling Drug, Inc., Thomasset Colors Div.

[a] In 1979, du Pont sold its paper dye operation to Mobay Chemical Corp., its Textile Dye Operations to Ciba Geigy Corp. and Crompton and Knowles Corp. and its ink dye operation to Morton-Norwich.

[b] In 1978, GAF Corp. sold its dye and pigment operations to BASF Wyandotte Corp.

Table 9

PRODUCERS OF DYES AND PIGMENTS BASED ON BENZIDINE AND ITS CONGENERS

C.I. No.	C.I. Name
Fabricolor Incorporated	
30235	Direct black 38
22590	Direct blue 2
30295	Direct green 6
--	Resin F. black WP
30145	Direct brown 95
30120	Direct brown 154
22610	Direct blue 6
22245	Acid red 85
35660	Direct brown 31
22120	Direct red 28
36300	Direct brown 74
22311	Direct brown 2
22130	Direct orange 8
30245	Direct black 4
22310	Direct red 1
30280	Direct green 1
30140	Direct brown 6
--	Direct blue 80
23155	Direct blue 98
--	Direct blue 100
23500	Direct red 2
American Color & Chem. Co.	
22910	Acid yellow 42
--	Direct blue 80
24410	Direct blue 1
24411	Direct blue 76
23500	Direct red 2

C.I. No.	C.I. Name
Mobay Chem. Corp., Verone Dyestuff Div.	
23266	Acid red 111
24400	Direct blue 15
--	Direct blue 160
Harmon Colors Corp.	
21200	Pigment red 41
21090	Pigment yellow 12
21095	Pigment yellow 14
21105	Pigment yellow 17
21110	Pigment orange 13
21115	Pigment orange 34
21120	Pigment red 38
21160	Pigment orange 16
Toms River Chemical Corp.	
23850	Direct blue 14
24401	Direct blue 218
--	Direct blue 80
23155	Direct blue 98
24410	Direct blue 1
--	Direct blue 160
23635	Acid red 114
23500	Direct red 2
23630	Direct red 39
23797	Direct blue 25
--	Acid red 167

Table 9 (Continued)

C.I. No.	C.I. Name
Atlantic Chemical Corp.	
24140	Direct blue 8
37235	Azoic diazo component 48
24175	Direct blue 151
--	Direct brown 230
23365	Direct orange 6
22890	Acid red 97
24401	Direct blue 218
--	Direct blue 80
23155	Direct blue 98
24410	Direct blue 1
24411	Direct blue 76
--	Direct blue 100
23635	Acid red 114
23500	Direct red 2
23797	Direct blue 25
--	Acid red 167
Synalloy Corp., Blackman-Uhler Chemical Div.	
--	Azoi black composition 4
37610	Azoic coupling component 5
37090	Azoic diazo component 32
21095	Pigment yellow 14
21100	Pigment yellow 13
21115	Pigment orange 34
--	Azoic blue composition 3
37575	Azoic coupling component 3
37558	Azoic coupling component 14
37010	Azoic diazo component 3

C.I. No.	C.I. Name
E. I. du Pont de Nemours & Co., Inc.	
24400	Direct blue 15
24401	Direct blue 218
Hercules, Inc.	
21096	Pigment yellow 55
21090	Pigment yellow 12
21095	Pigment yellow 14
21105	Pigment yellow 17
21100	Pigment yellow 13
21110	Pigment orange 13
21160	Pigment orange 16
GAF Corporation	
--	Azoic blue composition 3
23630	Direct red 39
21095	Pigment yellow 14
24401	Direct blue 218
--	Direct blue 80
23155	Direct blue 98
24410	Direct blue 1
24400	Direct blue 15
United Merchants & Manufacturers, Inc. Roma Chemical Div.	
21160	Pigment orange 16
21090	Pigment yellow 12
21095	Pigment yellow 14
21105	Pigment yellow 17
21115	Pigment orange 34

Table 9 (Continued)

C.I. No.	C.I. Name
Crompton & Knowles Corp. Dyes & Chemical Div.	
--	Direct blue 160
24411	Direct blue 76
23635	Acid red 114
--	Direct blue 80
23155	Direct blue 98
American Hoechst Corp., Industrial Chemicals Div.	
21160	Pigment orange 16
21090	Pigment yellow 12
21095	Pigment yellow 14
21105	Pigment yellow 17
21100	Pigment yellow 13
Binney and Smith, Inc.	
21160	Pigment orange 16
21095	Pigment yellow 14
Ridgway Color & Chemicals	
21090	Pigment yellow 12
21095	Pigment yellow 14
21100	Pigment yellow 13
21110	Pigment orange 13
21105	Pigment yellow 17
Sandoz, Inc., Colors & Chemicals Div.	
21095	Pigment yellow 14
21110	Pigment orange 13
21115	Pigment orange 34
Pfister Chemical Works	
37575	Azoic coupling component 3
Industrial Color, Inc.	
21100	Pigment yellow 13
21090	Pigment yellow 12
21095	Pigment yellow 14
21105	Pigment yellow 17
Apollo Colors, Inc.	
21090	Pigment yellow 12
21100	Pigment yellow 13
21095	Pigment yellow 14
Chemetron Corp., Pigments Div., Subsid. of Allegheny Ludlum Industries, Inc.	
21090	Pigment yellow 12
21095	Pigment yellow 14
21105	Pigment yellow 17
21100	Pigment yellow 13
21110	Pigment orange 13
Borden, Inc., Printing Inks Div.,	
21090	Pigment yellow 12

Table 9 (Concluded)

C.I. No.	C.I. Name
BASF Wyandotte Corp.	
22890	Acid red 97
24410	Direct blue 218
--	Direct blue 80
23155	Direct blue 98
24410	Direct blue 1
24400	Direct blue 15
37575	Azoic blue composition 3
23630	Direct red 39
Inmont Corporation	
21180	Pigment blue 25
21090	Pigment yellow 12
21095	Pigment yellow 14
21105	Pigment yellow 17
21110	Pigment orange 13
21096	Pigment yellow 55
Harshaw Chemical Co.	
21120	Pigment red 38
21090	Pigment yellow 12
21095	Pigment yellow 14
21105	Pigment yellow 17
21110	Pigment orange 13
21160	Pigment orange 16
Alliance Chemical Corp.	
37558	Azoic coupling component 14
37010	Azoic diazo component 3
--	Azoic blue composition 3
Galaxie Chemical Corp.	
21180	Pigment blue 25
21090	Pigment yellow 12
21095	Pigment yellow 14
21105	Pigment yellow 17
21100	Pigment yellow 13
21110	Pigment orange 13
21115	Pigment orange 34
21160	Pigment orange 16
Sun Chemical Corp., Pigments Div.	
21120	Pigment red 38
21090	Pigment yellow 12
21095	Pigment yellow 14
21105	Pigment yellow 17
21100	Pigment yellow 13
21110	Pigment orange 13
Sterling Drug, Inc.	
Hilton Davis Chemical Co.	
21160	Pigment orange 16
21090	Pigment yellow 12
21095	Pigment yellow 14
21100	Pigment yellow 13
21105	Pigment yellow 17
21115	Pigment orange 34
Indol Chemocal Co., Inc.	
21105	Pigment yellow 17
21115	Pigment orange 34
H. Kohnstamm & Co., Inc.	
21110	Pigment orange 13

Table 10

ESTIMATED TOTAL QUANTITY OF INTERMEDIATES IN SOLID AND AQUEOUS-SOLID WASTES FROM THE MANUFACTURE OF DYES AND PIGMENTS BASED ON BENZIDINE AND ITS CONGENERS

Intermediate	Solid Wastes (kg/yr)	Aqueous-Solid Wastes (kg/yr)
3,3'-Dichlorobenzidine	5,900	7,800
Acetoacetanilide	4,200	61,000
o-Acetoacetotoluidide	1,100	16,000
o-Dianisidine	560	760
1-Amino-8-hydroxy-3,6-naphthalene disulfonic acid (H acid)	510	8,400
o-Acetoacetanisidide	470	6,800
Hydrazobenzene	390	-
Benzidine	-	540
Aniline	190	3,200
m-Phenylenediamine	190	3,100
2,4-Acetoacetoxylidide	170	2,600
Phenol	120	1,900
o-Tolidine	89	120
3-Methyl-1-phenyl-5-pyrazolone	86	1,300
2-Hydroxy-3,6-naphthalene disulfonic acid (G acid)	83	1,400
p-Toluene sulfonyl chloride	80	1,312
N-Phenyl-7-amino-4-hydroxy-2-naphthalene sulfonic acid (N-phenyl-J acid)	62	1,000
1-Hydroxy-3,8-naphthalene disulfonic acid	62	1,000
6-Amino-4-hydroxy-2-naphthalene sulfonic acid (gamma acid)	56	910
Salicylic acid	56	890
2,4-Diaminotoluene	30	480
1-Amino-4-naphthalene sulfonic acid (Naphthoic acid)	29	460
p-Nitroaniline	25	400
4-Amino-5-hydroxy-1,3-naphthalene disulfonic acid (Chicago acid)	24	3,400
3-Methyl-1-p-tolyl-5-pyrazolone	24	420
Resorcinol	19	310

Table 10 (concluded)

ESTIMATED TOTAL QUANTITY OF INTERMEDIATES IN SOLID AND AQUEOUS-SOLID WASTES FROM THE MANUFACTURE OF DYES AND PIGMENTS BASED ON BENZIDINE AND ITS CONGENERS

Intermediate	Solid Residues (kg/yr)	Aqueous-Solid Wastes (kg/yr)
4-Aminobenzene sulfonic acid (sulfanilic acid)	17	270
2-Amino-1-phenol-4-sulfonic acid	17	280
3-Methyl-2-hydroxybenzoic acid (2,3-cresotic acid)	17	266
o-Phenylsulfonyl-2R-acid	9	140
4,8-Diamino-2,6-naphthalene disulfonic acid	8	120
1-Amino-6-naphthalene sulfonic acid (1,6-Cleve's acid)	8	120
1-Amino-7-naphthalene sulfonic acid (1,7-Cleve's acid)	8	120
3-Carbethoxy-1-phenyl-5-pyrazolone	5	77
2,2'-Dichlorobenzidine	4	5
Ethyl chloride	4	-
1,8-Dihydroxy-3,6-naphthalene disulfonic acid (Chromotropic acid)	3	41
3-Hydroxy-2-naphthalene carboxylic acid	3	41
2-Naphthol	3	130
1-Hydroxy-4-naphthalene sulfonic acid	2	32
1-Hydroxy-3,6-naphthalene disulfonic acid	1	16
7-Amino-4-hydroxy-2-naphthalene sulfonic acid (J acid)	1	16
3-Hydroxy-2-naphthanilide	1	11
p-Acetoacetotoluidide	1	11
2,4-Diaminobenzene sulfonic acid	1	16
2,6-Diamino-m-toluene sulfonic acid	1	16
Ethyl acetoacetate	1	16
m-Tolidine	1	1

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Appendix A

EXAMPLE OF MULTISTAGE PROCESS FOR A COMPLEX DYE

For many azo dyes, two or three stages of diazotization and coupling are required. Other types of reactions may also be required for these dyes, and they are performed in either the coupling or diazotization reactors. An intricate piping system is provided to interconnect the various diazotization and coupling reactors, and the filter presses. Some recipes call for the clarification of certain solutions or reaction intermediates, and clarifying filters are provided for this.

As an example of the processes used for manufacturing most of the benzidine-based dyes and pigments, Figure A-1 shows the steps necessary for producing one complex dye--Direct Green 1 (Colour Index No. 30280). The ingredients are added at each stage in the clockwise order of the arrows. This process consists of two diazotizations and three coupling reactions involving four organics--benzidine, H acid, aniline, and phenol. Benzidine is converted to the tetrazonium salt, H acid is coupled to one diazonium group on the benzidine, aniline is diazotized and coupled to the H acid, and finally phenol is coupled to the other diazonium group remaining on the benzidine. Figure A-2 shows the representative chemical reactions at each step, assuming that the reactions are complete and no by-products are formed.

The detailed recipe for producing Direct Green 1, which was adapted from the BIOS (1945) reports, is as follows:

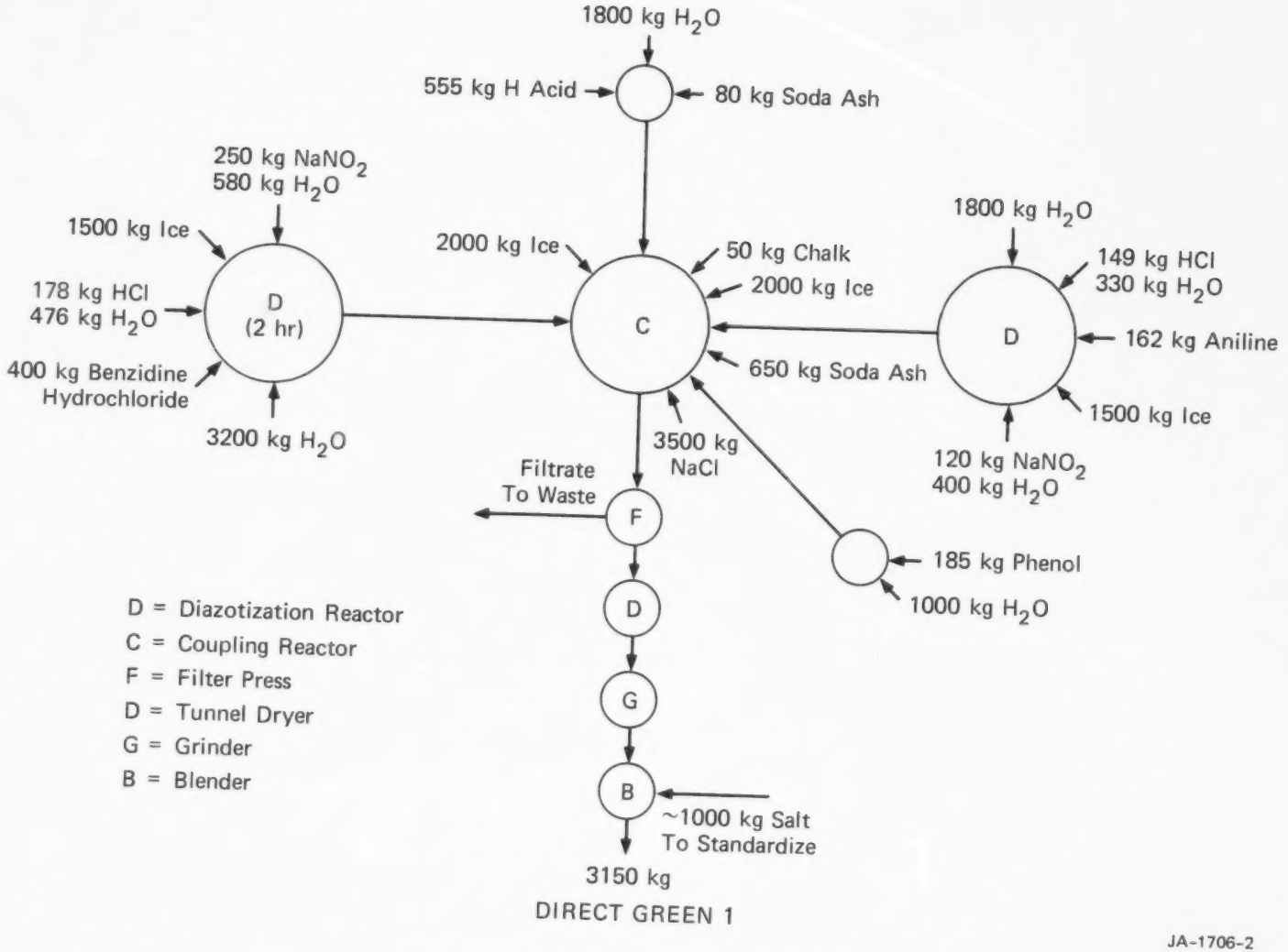

FIGURE A-1 STEPS REQUIRED FOR PRODUCTION OF DIRECT GREEN 1

(Components added in clockwise order.)

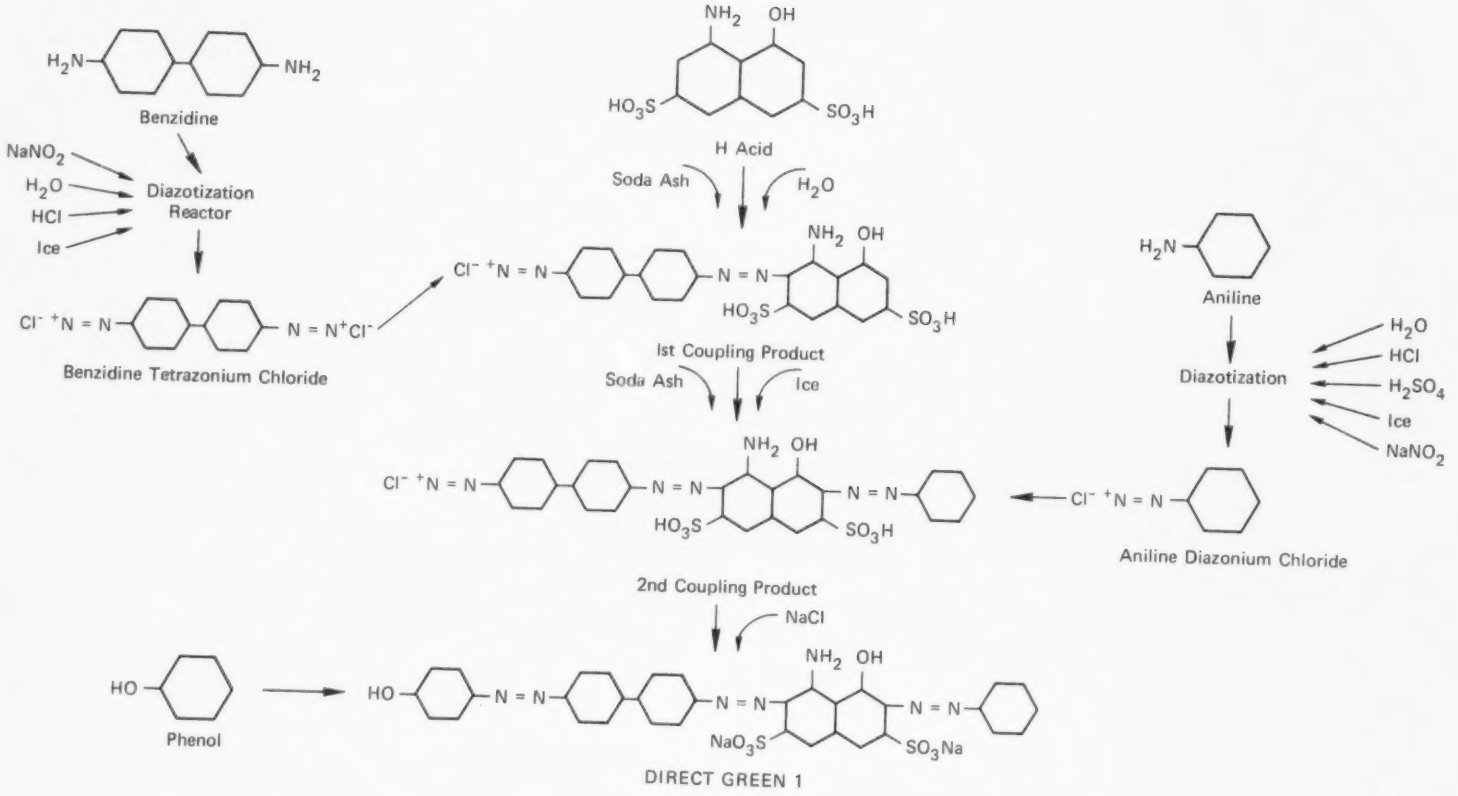

FIGURE A-2 REPRESENTATIVE CHEMICAL REACTIONS IN THE MANUFACTURE OF DIRECT GREEN 1

Stir 400 kg benzidine hydrochloride in 3,200 liters water in a diazotization reactor, add 500 liters hydrochloric acid, and stir overnight. Cool to 0°C with 1,500 kg ice; add 250 kg sodium nitrite as a 30% solution (temp 0°-4°C, volume 5,000 liters). Diazotization should be complete in two hours.

For the first acid coupling (on the acid side), transfer to a 12,000-liter vessel containing 1,500-2,000 kg ice. Stir 555 kg H acid into 1,800 liters water at 40°C and dissolve (by dusting in) 80 kg soda ash (volume 2,500-3,000 liters). Run the H acid into the tetrazonium salt over two hours with rapid stirring (temp 0°C, volume 9,000 liters). Stir slowly for three hours, then add slowly 25 kg powdered chalk and later that night 25 kg more. The next day the batch should give a faint blue test on Congo red, and there should be a slight excess of H acid. Add more chalk if the coupling is not complete. Run into a 30,000-liter coupling vessel.

In a diazotization reactor, dissolve 162 kg aniline in 1,800 liters water with 420 liters hydrochloric acid or 310 liters 40°Be sulfuric acid; add 1,500 kg ice. Diazotize at 0°C by adding 120 kg sodium nitrite as a 30% solution (volume 3,500 liters). In a separate reactor dissolve 185 kg phenol in 1,000 liters water at 70°C by adding 100 liters 50% caustic soda solution.

Add 2,000 kg ice to the first coupling product, then add the aniline diazonium salt, then, immediately and as rapidly as possible, add 650 kg solid soda ash, keeping the batch at 0°C. After two hours, the aniline diazonium salt should be gone, or almost so. Then add the phenol solution. The batch gets very thick and the stirring may have to be stopped. Allow to stand overnight to complete the reaction and permit crystal growth. Next morning heat to 65°C with direct steam, add 3,500 kg salt, stir two hours while cooling to 50°C, and filter. The filtrate should be a pale blue-black color. Dry at 95°C, grind, and standardize with salt in a blender.

Yield is about 2,000 kg, before standardization. After blending, a typical final product yield is 3150 kg.

Note that this recipe calls for a trace excess of H acid after the first coupling step is stopped. Since benzidine was added in a molar excess (.96 mole H acid: 1 mole of benzidine) when only a trace of H acid remains, the unreacted benzidine tetrazonium salt accounts for ~ 15 kg. The final volume of the mother liquor is at least 15,000 liters or greater, which means that benzidine tetrazonium salt concentration could be 1000 ppm.

Levels this high are not expected because the benzidine tetrazonium salt may couple to the phenol added later and will also decompose to by-products that were discussed in Section 3.

The recipe also calls for the second coupling reaction to be complete, so no excess aniline diazonium salt or first coupling product should remain. The addition of phenol and further reaction leads to the dye product. The recipe calls for a 13% excess of phenol or ~ 40 kg excess, giving a final phenol concentration in the mother liquor of less than 3000 ppm if coupling is complete.

Appendix B

ESTIMATION OF BY-PRODUCTS AND UNREACTED INTERMEDIATES PRODUCED BY DYE AND PIGMENT MANUFACTURE

It is not possible to calculate the amounts of by-products and unreacted intermediates that are produced for each dye and pigment. Recipes reflecting current practice are not available, and rates for conversion to the numerous possible by-products have not been determined. A procedure was developed to obtain order of magnitude estimates of the amounts of unreacted intermediates and by-products that might be present in the reaction mixture after all of the coupling reactions were completed. The procedure was developed using Direct Green 1 as an example and then generalized to cover all of the dyes and pigments based on benzidine and its congeners. The final result was a set of emission factors for these dyes and pigments that expressed the amount of unreacted intermediate and by-product in the final reaction mixture (the mother liquor) as a percentage of the final standardized product. These emission factors can be used to estimate the amounts of unreacted intermediate and by-product produced without working out in detail the stoichiometry of all of the coupling reactions and can be applied to dyes and pigments where the complete recipe is not available. Several assumptions were required. It was assumed that each intermediate, except benzidine or its congeners, was added to the reaction at a 5% excess. It was also assumed that during each reaction step 2% of the diazonium salt present in the vessel decomposes and terminates (Gerber, 1980). Production of other by-products such as N-nitrosamines was neglected.

When other intermediates required diazotization in order to couple an amine to the growing dye or pigment molecule, it was assumed that diazotization was not complete and that the excess intermediate added remained in its original form. It would be possible to use an alternative assumption here, that is, to assume complete diazotization and subsequent decomposition of unreacted diazonium salt to the hydroxide form or to other by-products such as the N-nitrosamine. However, this

assumption was not used because there was no information that suggested it to be more probable than the one that was used.

The consequences of these assumptions are worked out in Table B.1,. The recipe used for Direct Green 1 is slightly different from the one given for this dye in Appendix A because that recipe did not utilize 5% excess of all ingredients except benzidine. The net results are 31 kg of unreacted intermediates (4.3% of the organic dye yield) and 37 kg of by-products (5.2% of the organic dye yield). To generalize this result to other dyes, each of the three intermediates (benzidine is excluded) was assumed to contribute equally to the 31 kg, which means 10.3 kg for each intermediate or 1.44% of the organic dye product for each intermediate. The percentage was rounded up to 1.5%.

To generalize this result even further, it was assumed that for any given dye or pigment, each intermediate, regardless of the number of intermediates actually required (except benzidine and its congeners) might be present in an unreacted form at levels equivalent to 1.5% of the organic dye product. For dyes, this is equivalent to 0.75% of the final standardized product. For pigments, this is equivalent to 1% of the average final product. The 5.2% yield of by-products on an organic dye basis was rounded to 5% and calculated to be equivalent to a 2.5% yield on a final standardized dye product basis and a 3.5% yield on an average pigment product basis.

Table B.1

EXAMPLE CALCULATION OF BY-PRODUCTS AND UNREACTED INTERMEDIATES FROM PRODUCTION OF DIRECT GREEN 1

Material	Weight (Kg-mole)	Weight (Kg)
Starting materials		
Benzidine ($H_2N\emptyset\emptyset NH_2$)*	1.0	222
H Acid (h)	1.05	320
Aniline ($\emptyset NH_2$)	1.05	98
Phenol ($\emptyset OH$)	1.05	99
		739
Products after first coupling		
Benzidine	trace	-
H Acid	0.05	16
Product ($C\bar{l}^{+}N\emptyset\emptyset NNH$)	0.98	587.5
Terminated product 1 ($HO\emptyset\emptyset NNH$)	0.02	11
Products after second coupling		
Benzidine	trace	-
H Acid	0.05	16
Aniline	0.07	6.5
Product ($C\bar{l}^{+}NN\emptyset\emptyset NNhNN\emptyset$)	0.96	685.5
Terminated product 2 ($HO\emptyset\emptyset NNhNN\emptyset$)	0.02	13
Terminated product 1	0.02	11
Products after third coupling		
Benzidine	trace	-
H Acid	0.05	16
Aniline	0.07	6.5
Phenol	0.09	8.5
Product ($HO\emptyset NN\emptyset\emptyset NNhNN\emptyset$)	0.94	715.3
Terminated product 2	0.04	26
Terminated product 1	0.02	11
Organic dye yield		715.3 kg
Total unreacted intermediates		31 kg
Total by-products		37 kg

*$\emptyset$ indicates an aromatic ring.